VOLUME XXXVII JULY 1958 No. 3

OHIO STATE UNIVERSITY
AUG 6 1958
LIBRARY

FUEL

A QUARTERLY JOURNAL OF FUEL SCIENCE

Editor
SIR ALFRED EGERTON, F.R.S.

Deputy Editor (U.S.A.)
C. H. RIDER

Editorial Committee

I. G. C. Dryden
F. H. Garner, O.B.E.
R. H. Griffith
W. Idris Jones, O.B.E.
J. R. Joyce
I. G. King, O.B.E.
S. Lacey
D. M. Newitt, F.R.S.
A. Parker, O.B.E.
M. W. Thring

BUTTERWORTHS SCIENTIFIC PUBLICATIONS

XUM

The following articles were published in the June issue of **COMBUSTION AND FLAME,** *the Quarterly Journal of the COMBUSTION INSTITUTE*

Page

EFFECT OF PRESSURE ON TURBULENT BURNING VELOCITY. *B. Fine* 109

SEPARATION OF THE PRODUCTS OF COOL FLAME OXIDATION OF PROPANE. *C. R. Yokley and R. E. Ferguson* 117

THE DETONATABILITY ENVELOPE OF GASEOUS FUMING NITRIC ACID–*n*-HEPTANE–NITROGEN MIXTURES AS A FUNCTION OF INITIAL PRESSURE. *R. L. Potter and D. H. Wayman* 129

THE HYDRAZINE FLAME. *M. Gilbert* 137

KINETICS OF HYDRAZINE DECOMPOSITION IN A LAMINAR NON-ISOTHERMAL FLOW. *M. Gilbert* 149

THE COMBUSTION OF THE BUTANE-2,3- AND 1,4- DIOLDINITRATES AND SOME ALDEHYDE–NITROGEN DIOXIDE MIXTURES. *J. Powling and W. A. W. Smith* 157

INVESTIGATIONS ON THE INFLAMMABILITY RANGES OF METHANE–AIR AND BUTANE–AIR MIXTURES IGNITED BY ELECTRIC SPARKS. *Gisèle Dalmai* 171

GASEOUS NITRIC ACID–HYDROCARBON FLAMES. *J. Mertens and R. L. Potter* 181

SOME RECENT DEVELOPMENTS CONCERNING FREE RADICALS (A REVIEW) *G. J. Minkoff* 193

RECENT DEVELOPMENTS AND NOTES. *W. A. Kirkby* 208

PUBLICATION 224

LETTERS TO THE EDITORS: LAMINAR FLAME THEORY. *J. Adler and D. B. Spalding;* SEMI-EMPIRICAL DETERMINATION OF GAS CHARACTERISTICS IN THE CHAPMAN–JOUGUET STATE. *N. Manson* 225

The Infra-red Spectra of Coal and Some Coal Derivatives

W. DEN HERTOG and N. BERKOWITZ

Infra-red spectra of three Western Canadian coals and of a series of solvent extracts, humic acids, humates and pyridine-extract fractions are reported. The spectra were determined in order to assess more closely the applicability of i.r. spectroscopy to coal-like materials and to explore the possibility of establishing some unifying characteristics of solvent extacts, but were generally found to be so diffuse as to render detailed analysis impossible. Spectra containing more diagnostic absorptions than those of coal were in fact only found with a few extracts isolated with very weak solvents; extracts produced with strong solvents, or by the action of relatively weak solvents on immature coals, tended to yield diffuse spectra that were closely similar to those of coal. On the other hand, i.r. spectroscopy can assist in clarifying the major structural changes that occur when coal is converted into humic acids and humates; and its application, together with x-ray diffraction methods, to fractions of a pyridine-extract, has yielded results that suggest the pyridine-extract to constitute a two-component system. One of these components appears to be particularly rich in C=H-containing structures, and the other in non-aromatic C—H.

I. INTRODUCTION

RECENT publications[1–4] dealing with the infra-red (i.r.) spectroscopy of coal suggest strongly that a continuation of such studies with presently available means is unlikely to reveal much that is new. Even the most painstakingly determined coal spectra seem incapable of providing more than qualitative information about a few functional groups; and unless there are far-reaching advances in experimental technique, the conclusion that the method will *remain* of restricted utility is inescapable. Yet, despite this general appreciation, there would appear to be several areas in which some further exploration by i.r. spectroscopy may, *prima facie*, be warranted. One of these is the precise relationship between coal and the various derivatives that can be prepared from it by, for example, oxidation and solvent extraction. In the absence of definite information to the contrary, some of these derivatives may well be expected to prove rather more tractable than the unresolved parent coal.

The investigations summarized in the following pages deal therefore with several separate but intimately related topics. The i.r. study of the three coals (Section II) was intended to provide the necessary background. Examination of solvent extracts (Section III) was aimed at elucidating similarities and dissimilarities between such extracts and at the possible establishment of some unifying generalizations. Spectra of humic acids and of some humates (Section IV) were determined in order to assess structural changes due to oxidation and to explore changes in intensity and position of the 6·2μ band of the coal spectrum; and the work with pyridine–water mixtures (Section V) was prompted by the thought that such mixtures might achieve a partial resolution of coal extracts without introducing complications arising from the use of several *different* solvents.

LORD HALL LIBRARY

With the possible exception of the work described in Section V, none of these topics is novel; in one way or another, all have in fact been repeatedly investigated in the past. But in each case, the present position is still so far from being established that a re-examination requires little justification.

The i.r. spectra reported in this communication were recorded with a Perkin–Elmer model 21 double-beam spectrometer in which samples were examined (*a*) in the form of thin smears on sodium chloride discs, (*b*) as Nujol mulls, or (*c*) in potassium bromide pellets. The choice between these forms was generally determined by the nature of the substance under test, e.g. by whether it was brittle or resinous, and by the information desired. For example, if absorption due to non-aromatic C—H was considered unimportant for the evaluation of a particular spectrum, recourse was made to the simpler mull-technique. On the other hand, where potassium bromide pellets were employed, an effort was made to obtain spectra capable of at least semi-quantitative interpretation; a sample concentration of 0·2 per cent and a pellet thickness of *ca.* 0·8 mm proved very suitable for this purpose. In all cases, moreover, care was taken to dry thoroughly all materials under appropriate non-oxidizing conditions before submitting them to i.r. analysis.

The x-ray diffraction patterns from which the crystallite dimensions reported in Section V were calculated, were obtained with a Norelco x-ray spectrometer coupled to a strip chart recorder. Cu K_α radiation (with $\lambda = 1{\cdot}5402$ Å) was used, and scanning was carried out over the range $\theta = 1°$ to 90° at 1° per minute. The dial settings on the spectrometer were: scale factor = 2; multiplier = 1·0; time constant = 8.

II. THE INFRA-RED SPECTRUM OF COAL

The i.r. spectra of the three coals selected for closer examination within the present study (cf. *Table 1*) are reproduced in *Figure 1*. All three spectra were recorded with 0·8 mm thick potassium bromide discs containing 0·2 per cent of finely ground coal; and since the spectrometer was in each instance set to give 100 per cent transmission without the sample in the beam, they are directly comparable. As expected, however, they show no new features. In

Table 1. Analysis of coals

Coal No.	Description		Ash %	VM %	FC %	C %	H
1	*Lignite; Taylorton, Sask.*	(*a*)	8·2	40·6	51·2	67·8	4·5
		(*b*)	—	44·2	55·8	73·9	4·9
2	*Sub-bituminous coal; East Coulee, Alta.*	(*a*)	11·8	36·2	52·0	66·8	4·5
		(*b*)	—	41·0	59·0	75·7	5·1
3	*Low-volatile bituminous coal; Nordegg, Alta.*	(*a*)	6·2	15·7	78·1	85·4	4·1
		(*b*)	—	16·7	83·3	91·0	4·4

(*a*) Dry coal basis. (*b*) Dry, ash-free coal basis.
NOTE: All coals were freshly mined and stored in sealed jars under water until prepared for examination.

conformity with previous findings[1–6], diagnostic detail is severely limited, and the effect of coal maturation, i.e. the effect of an increase in rank, is reflected in only a few, rather generalized and already well-established spectral changes. There is thus a tendency towards progressively higher background absorption; absorption intensities of bands at (or near) 2·9μ and at 3·45, 3·52,

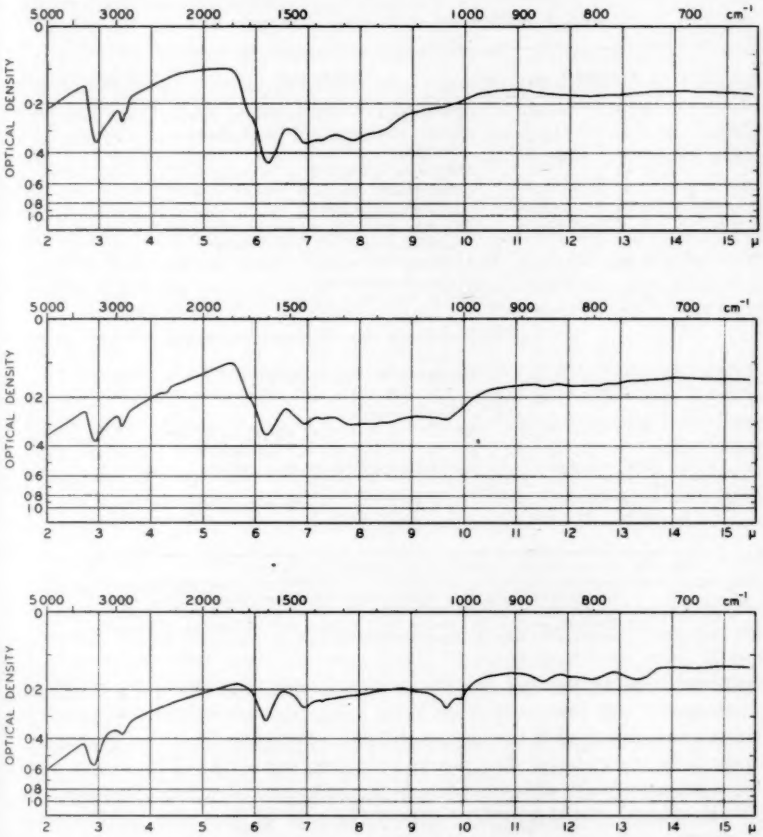


Figure 1. Infra-red spectra of coal. Coal No. 1—Top, No. 2—Middle, No. 3—Bottom

6·85 and 7·25μ decrease; and there is, especially in the case of the highest-rank coal (Coal No. 3), a marked intensification of absorption centring about 11·50, 12·40 and 13·32μ. The assignments to these bands, and a few explanatory notes, are given in *Table 2.*

Some more detailed comment, however, is merited here by two features of coal spectra which have been (and, to some extent, still are) the subject of considerable speculation and uncertainty.

The first of these is the very pronounced absorption observed in all coal spectra at or near 2·9μ. This absorption is generally considered to arise from O—H stretching vibrations and always indexed as such; but the possibility that N—H stretching vibrations contribute to it ought not, in our view, to be ignored. Unless a substantial part of the 2·9μ absorption is associated

Table 2. Assignments of absorption frequencies for coal

Frequency, μ	*Assignment*	*Note*
2·95	O—H (*and* N—H) *stretching vibrations. Evidence for strong hydrogen-bonding*	*A*
3·45, 3·52	*Stretching vibrations of non-aromatic (aliphatic, alicyclic and/or hydroaromatic)* C—H	
4·30 *Coal No. 2*	*Possibly spurious; due to inadequate cancellation of* CO_2 *absorption*	
5·90	*Carbonyl absorption; possibly due to sample oxidation*	
6·20	C=C *stretching vibrations; generally considered to be reinforced by absorption due to hydrogen-bonded quinoid* C=O	*B*
6·95, 7·25	*Symmetrical and asymmetrical bending vibrations of non-aromatic* C—H *groups*	*C*
9·65 *Coal No. 2*	Si=O	*Note that these bands do not, as a rule, occur in solvent extract spectra*
9·95 *Coal No. 3*	*Kaolinite*	
11·50, 12·40, 13·35	*Aromatic* C—H '*out-of-plane*' *deformations*	

NOTE *A*: Hydroxyl groups are believed to be primarily phenolic[9].
B: Since the intensity of this band appears to be relatively independent of coal rank, nitrogen-containing rings (such as occur in pyridines and quinolines) may be a more likely cause of the reinforcement[10].
C: The 6·95μ band is here shifted from its more normal position at 6·85μ, but occurs at the latter wavelength in the spectra of coal *extracts*.

with moisture in the test sample or in the potassium bromide—and this contingency will obviously have been minimized by careful drying of all substances employed in the i.r. examination—the intensity of the band would seem to be rather larger than can be accounted for by O—H structures only. As a matter of fact, with Coal No. 3, the percentage of oxygen available for O—H groups[7] would equal, or actually be smaller than, the percentage of nitrogen.

The second point relates to the carbonyl absorption which manifests itself as a shoulder on the lower wavelength side of the 6·2μ band in the spectra of Coals Nos. 1 and 2. In attributing these absorptions to C=O groups introduced into the coals by accidental oxidation during preparation, we follow precedent[8], but the evidence upon which this interpretation rests is somewhat circumstantial and not entirely satisfactory. If the absence of separate carbonyl absorption in unoxidized coal is considered to be due to hydrogen-bonding of (quinoid) C=O—a mechanism that would mask the appropriate absorption by shifting it into the dominant 6·2μ band—instances

in which such C=O absorption does appear at characteristically lower wavelengths could conceivably be accounted for by assuming *incomplete* hydrogen-bonding in the fresh coal, or by postulating a partial disruption of such bonding during preparation. Though not of direct relevance in the present context, this point seems to merit further and more detailed investigation than has already been undertaken.

III. THE INFRA-RED SPECTRA OF COAL EXTRACTS

In the course of a series of preliminary experiments, designed to establish appropriate extraction conditions, it was observed that the i.r. spectrum of a coal extract was remarkably insensitive to the manner in which the extract was prepared. Spectra of extracts obtained in open Soxhlet apparatus at the b.pt of the solvent were indistinguishable from the spectra of extracts prepared at room temperatures by shaking coal and solvent in a sealed, nitrogen-filled flask. No significant differences could be found between the spectra of extracts prepared in open and nitrogen-sealed Soxhlet apparatus; and, finally, the solid (regenerated) room-temperature extracts were shown to suffer no irreversible changes detectable by i.r. spectroscopy when they were gently heated in air to temperatures of about 150°C*.

In the light of these observations, the i.r. spectra of Soxhlet extracts (prepared from dry, −65 mesh coal at the b. pt of the solvent) were considered to afford fairly reliable material for investigation. The experimental evidence indicates quite unequivocally that such extracts represent relatively stable complexes not seriously affected by access of air or gentle heat, and that extraction of any one coal with a particular solvent appears to isolate fairly definite—or, at least, spectroscopically highly reproducible—entities.

On the other hand, it soon became clear that generalizations about the nature and spectroscopic properties of solvent extracts of coal were complicated, if not indeed rendered altogether impossible, by several complex physical interactions. Two effects in particular, one stemming from the solvent and the other from the coal, could be recognized with some clarity, and it may be helpful to summarize these before entering upon a discussion of the individual spectra.

The type example illustrative of a more or less unobscured 'solvent effect' appears to be given by the extraction of a *mature* (*medium or low-volatile*) *bituminous coal* with a series of solvents. In such a case, solvents tend to range themselves broadly into one of two classes, some (e.g. benzene, toluene, xylene, acetone, chloroform) yielding extracts whose spectra show *very much more* structural detail than the spectrum of the parent coal, and others (e.g. methanol, ethanol, quinoline, pyridine, ethylene diamine) producing extracts with essentially coal-like spectra. It is therefore possible here to make a *prima facie* distinction between selective and non-selective solvents, i.e. between solvents yielding extracts possessing 'detailed" and 'diffuse' spectra respectively. A considerable element of arbitrariness attaches, of course, to so simple a dichotomy, and it must not be regarded as implying a rigid 'classification' of solvents. For example, when applying it to the extraction

* A notable exception to this statement, relating to the benzene-extract of Coal No. 3, is discussed at a later stage.

of a series of bituminous coals, the distinction becomes somewhat of an idealization since the boundary between selective and non-selective solvents may shift from one case to the next and at times be rather tenuous (see below). Nevertheless, both the distinction and the terminology adopted here seem to possess fundamental significance: the fact that (spectroscopically) selective solvents will, as a rule, only extract very small proportions of a bituminous coal ($\gtrsim$0·5 per cent) suggests—as do the extract spectra themselves—that they remove particular adventitious or 'admixed' components rather than coal material *per se*. The composition of extracts as deduced from, say, the benzene- and acetone-extract spectra (see below) support this point. In contrast, non-selective solvents, regardless of whether they extract much or relatively little, seem on the face of the available spectroscopic evidence to disperse 'whole coal', and the extract solutions have two properties in common: they are frequently optically unclear and they tend to be more or less unstable. They will, for example, commonly precipitate solid matter upon standing, even when air and light are excluded.

However, when extended to the extraction of *immature* coals, concepts of selectivity and non-selectivity tend to lose their practical significance. In the extraction of lignites and sub-bituminous coals, even weak solvents (which would behave 'selectively' towards bituminous coals) may occasionally disperse so much coal substance that the spectrum of the resultant extract becomes swamped and almost (or just) as featureless as the spectrum of the parent coal. The spectra of extracts prepared from the Saskatchewan lignite (see below) may be cited as cases in point: not only do the extract solutions (with the possible exception of the benzene solution) behave as colloidal dispersions, but spectral detail is progressively lost as the proportion of coal substance in the extract (as judged by the intensity of the 6·2μ absorption band) increases. In considering solvent extraction of a range of coals of different rank, allowance must consequently be made for a 'coal effect' which appears to depend upon the nature and state of aggregation of the coal under test, and which effectively opposes a uniform and definite distinction between selective and non-selective solvents. It seems at least probable that this coal effect becomes the more pronounced the lower the rank of the coal.

The recognition that the dividing line between selective and non-selective solvents will shift with coal rank and that spectral detail will be lost in proportion to the amount of dispersed coal substance in the extract, affords a simple picture of the action of solvents on coal and defines the areas in which i.r. spectroscopy remains a useful tool for the examination of solvent extracts. In terms of i.r. spectroscopy, the extraction process may be envisaged as involving, first, the removal of adventitious components, e.g. waxes and resins, which tend to produce a fairly well-defined, detailed spectrum, and, secondly, the progressive dispersal of part of the coal substance. 'Useful' spectra, in the sense of containing sufficient diagnostic details for profitable analysis, can therefore only be expected in two special cases, i.e. (*a*) when only the first stage can be completed, and (*b*) when extraction of adventitious components and the dispersal of coal substance occur as clearly consecutive events, and when the extraction is interrupted between the first and second stages. If

the two stages occur simultaneously—as will be the more usual event, especially with low-rank coals—the extract spectrum must be expected to be the more coal-like (and diffuse) the higher the ratio of dispersed coal substance to dissolved adventitious material. (If the amount of available adventitious material in a coal is very small, the extract spectrum may consequently be coal-like even if relatively little coal substance is dispersed.)

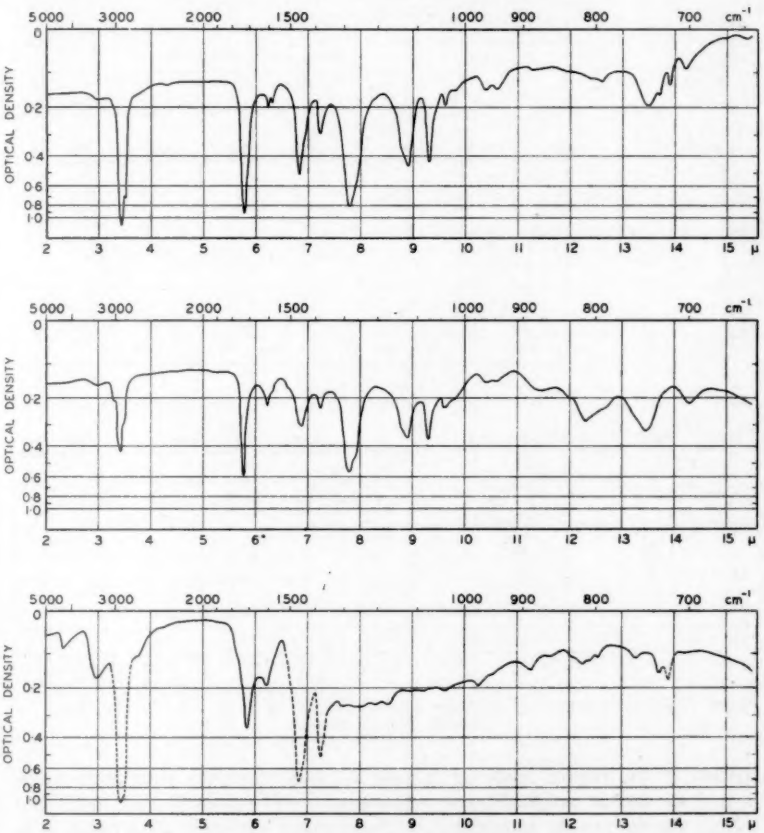


Figure 2. Infra-red spectra of benzene-extracts. Extract of Coal No. 2—Top, No. 3—Middle, No. 1—Bottom.
(Nujol absorptions are indicated by broken line.)

It is against this background that the extract spectra recorded in the course of the present study are most usefully viewed.

The apparent ability of selective solvents to extract specific coal components is perhaps best exemplified by a comparison of the spectra of benzene-, acetone- and chloroform-extracts prepared from Coals Nos. 2 and 3. The benzene-extract spectra of these two coals are shown in *Figure 2*. Unlike the

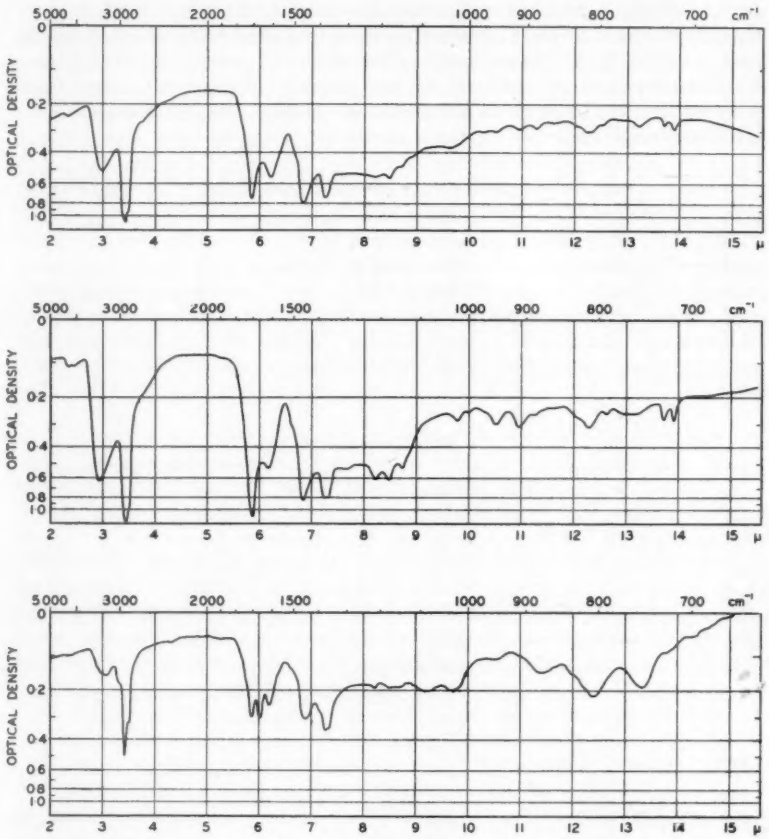


Figure 3. Infra-red spectra of acetone-extracts. Extract of Coal No. 1—Top, No. 2—Middle, No. 3—Bottom

spectra of the parent coals (cf. *Figure 1*), they show no absorption at or near 2·9μ; bands assigned to non-aromatic C—H (at 3·45, 3·52, 6·85 and 7·26μ) are all greatly intensified; a pronounced carbonyl absorption is in evidence at 5·78μ; the 6·25μ band is weakened and supplemented by absorption at 6·32μ; and several new bands appear at wavelengths above 7·5μ. Spectral analysis suggests that the C=O band at 5·78μ arises from aromatic ester carbonyls and that aromatic esters are responsible for further absorption bands centring about 7·80, 8·90 and 9·30μ*. The bands at 6·25 and 6·32μ

* When the benzene extract of Coal No. 3 is heated *in vacuo* to about 100°C, some devolatilization occurs and the spectrum of the residue is almost devoid of bands at 5·78, 7·80, 8·90 and 9·30μ. The devolatilized complex must therefore encompass structures absorbing at all four wavelengths. It might in this connection be noted that no such devolatilization occurs on heating the benzene-extracts of Coals Nos. 1 and 2, a fact that suggests that the maturation of coal may be accompanied by some form of depolymerization of aromatic esters. It is tempting to speculate as to how far such a process can be held responsible for the absence of 'resins' in high-rank coals.

are assigned to C=C structures, and absorption at 13·50μ indicates the presence of substituted benzene rings.

Spectra of the acetone- and (to a lesser extent) chloroform-extracts of Coals Nos. 2 and 3 (cf. *Figures 3* and *4*), on the other hand, resemble the benzene-extract spectra only in the *amount* of detail. For example, unlike the

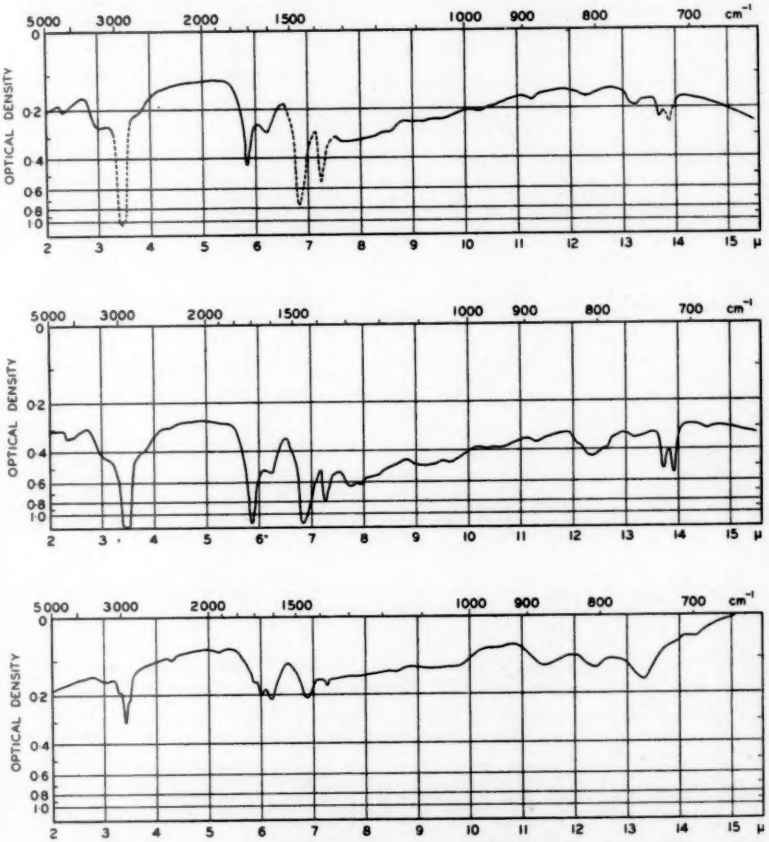


Figure 4. Infra-red spectra of chloroform-extracts. Extract of Coal No. 1—Top, No. 2—Middle, No. 3—Bottom.
(Nujol absorptions are indicated by broken line.)

benzene-extract spectra, they show fairly pronounced absorption at 2·9μ but none at 13·50μ; the carbonyl band is shifted to 5·87μ; and the general pattern assigned to aromatic esters has been replaced by a pattern indicative of *ketonic* structures. It is in this connection of interest that similar ketonic structures can be isolated from the Saskatchewan lignite (Coal No. 1) by

extraction with *benzene*. Acetone and chloroform lead to extracts possessing coal-like spectra.

An illustration of the nature of coal extracts prepared with non-selective solvents is afforded by the spectra of pyridine extracts, reproduced in *Figure 5*. From the standpoint of the coal chemist concerned with coal constitution,

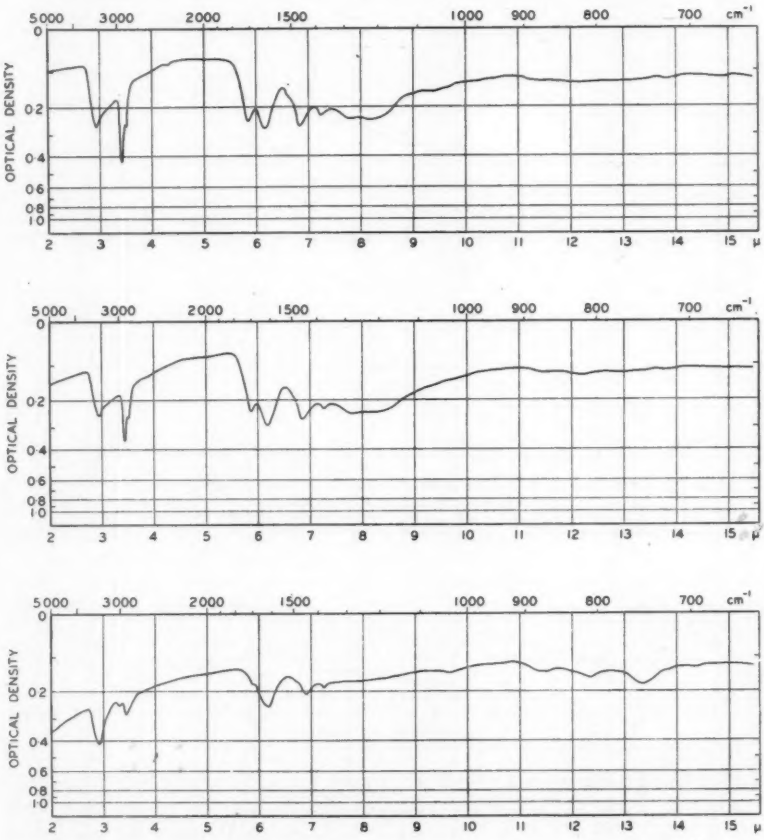


Figure 5. Infra-red spectra of pyridine-extracts. Extract of Coal No. 1—Top, No. 2—Middle, No. 3—Bottom

pyridine extracts, or extracts obtained with other 'strong' solvents, are for obvious reasons of considerably greater interest than the very small yields obtainable with selective solvents (when they act as such); but since pyridine and other strong solvents appear to cause random dispersal of coal substance, i.r. spectroscopy is fundamentally unsuitable for studying such extracts in any detail. In the specific case of the pyridine extract, for instance, the spectrum

differs from the spectra of the parent coals (cf. *Figure 1*) and of the pyridine-insoluble residues (cf. *Figure 6*) on only two, relatively minor, points: absorption at 2·9μ and bands assigned to non-aromatic C—H are somewhat enhanced, and a sharp, intense carbonyl band makes its appearance at about 5·87μ. Beyond concluding that the pyridine extract is not entirely identical

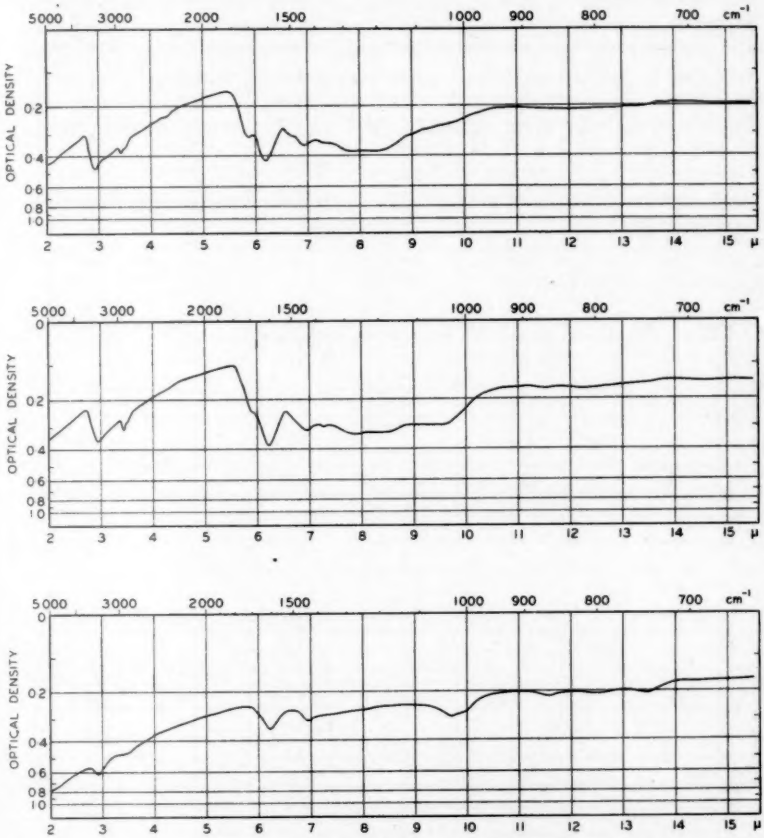


Figure 6. Infra-red spectra of pyridine-insoluble coal fractions. Insoluble fraction of Coal No. 1—Top, No. 2—Middle, No. 3—Bottom

with the parent coal, however, it is impossible to go. The structures comprising the extract as a whole, and the configurations causing seeming enrichment of the pyridine-extract in C=O, —OH, and non-aromatic C—H, remain as obscure as in the unresolved coal itself. The same applies to the i.r. spectra of extracts procured with other strong dispersing agents, e.g. quinoline and ethylene diamine; and it is equally true of the spectra of extracts prepared from immature coals with what would usually be considered

'weak' solvents. As already noted, spectra of extracts obtained from Coal No. 1 with acetone and chloroform are as diffuse and coal-like as the spectrum of the pyridine-extract prepared from Coal No. 3.

In connection with the pyridine-extract spectra shown in *Figure 5*, one comment might, however, usefully be made here. While the carbonyl shoulder

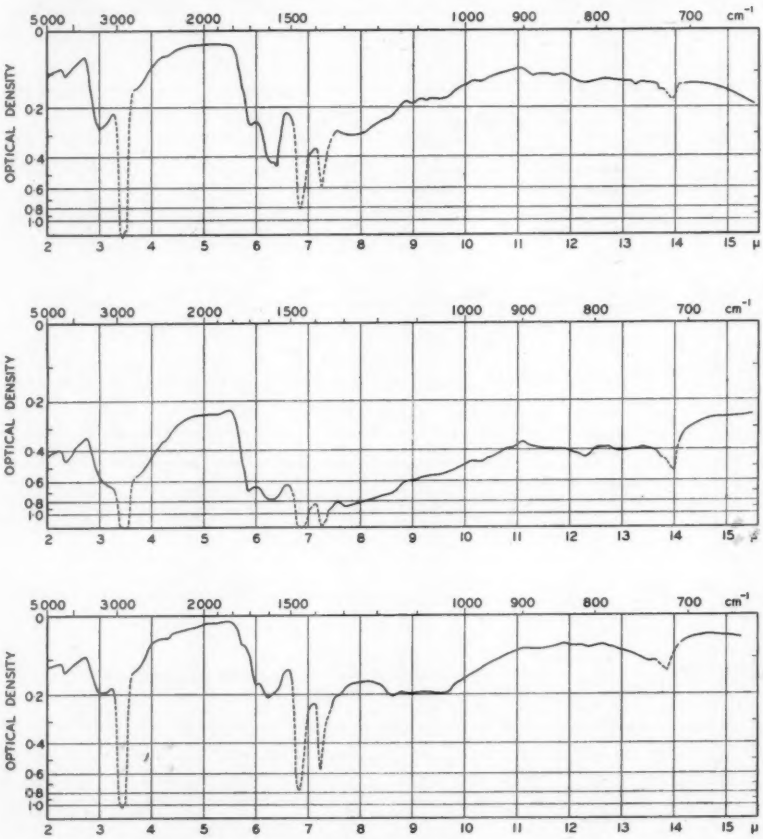


Figure 7. Infra-red spectra of methanol-extracts. Extract of Coal No. 1—Top, No. 2—Middle, No. 3—Bottom
(Nujol absorptions are indicated by broken line.)

of the coal spectra may be due to atmospheric oxidation of the sample, the strong C=O absorption found in the extract spectrum *cannot* be attributed to accidental oxidation. Oxidation sufficiently intense to cause the 5·87μ band would simultaneously cause far-reaching destruction of absorption due to non-aromatic C—H (cf. Section IV and *Figure 9*); and a material

balance, involving computation of the relative intensities of CH_2, CH_3 and C=O absorption for extract, residue and parent coal on the basis of extract yield is equally inconsistent with any significant oxidation during preparation and regeneration of the extract.

Coal-like extracts similar to those obtained by the use of pyridine or ethylene diamine appear, rather interestingly, also to be obtained with the lower alcohols (particularly methanol and ethanol). Extract *yields* are of course very much smaller than those recorded with 'strong' solvents, but despite this, the extract spectra—even when relating to extracts of a mature bituminous coal—are no more informative than the spectra of pyridine- or ethylene diamine-extracts. *Figure 7* illustrates this point. On the other hand,

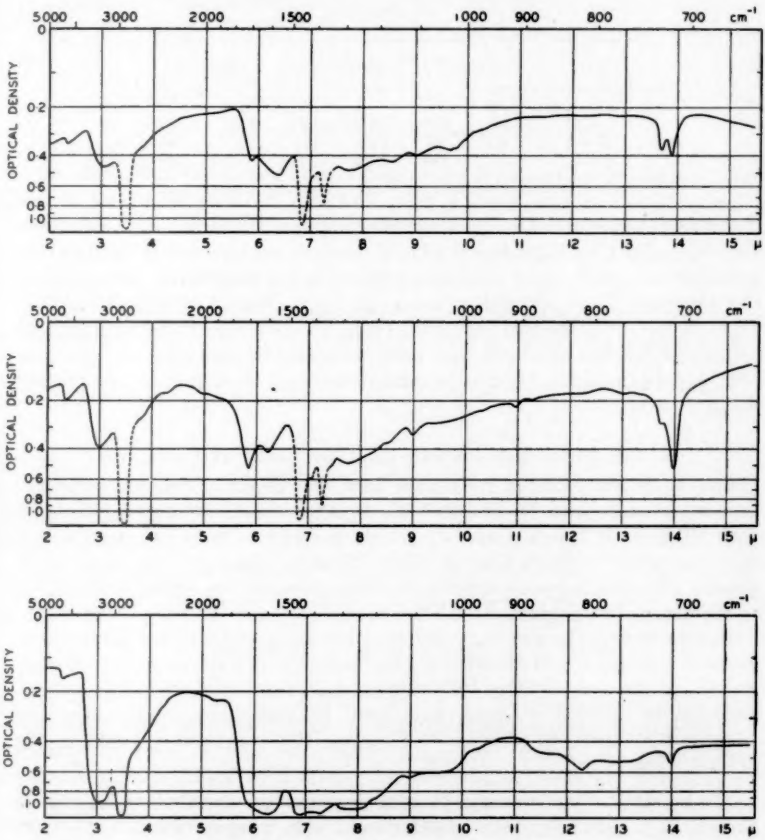


Figure 8. Infra-red spectra of fractions of a methanol-extract of Coal No. 2. Precipitate No. I—Top, Precipitate No. II—Middle, Solid residue—Bottom. (Nujol absorptions are indicated by broken line.)

methanol solutions occasionally exhibited a behaviour not observed with any other solutions (or dispersions) examined in the present study. For example, as Soxhlet extraction proceeded, a solid precipitate would form in the flask; and when this was later removed by centrifuging and the clear methanol solution partly condensed, a second precipitate would begin to settle out. In view of the possibility that these separations represented a form of fractional precipitation of the methanol-extract, tne two precipitates (I and II) and the solid residue obtained by complete evaporation of the solution (after removal of precipitate II) were examined separately. The resultant spectra, which refer to extract fractions from Coal No. 2, are shown in *Figure 8*. All three spectra are essentially coal-like, but several significant differences nevertheless

Table 3. Fractional precipitation of the methanol extract of Coal No. 2

	Precipitate I		*Precipitate II*		*Residue*	
Assignment	λ, μ	*E*	λ, μ	*E*	λ, μ	*E*
—OH	3·05	105	3·00	160	3·05	98
C=O	5·85	67	5·85	184	5·85	68
C=C	6·37	100	5·25	100	6·25	100

obtain between them. The spectrum of precipitate II shows, thus, a considerably enhanced C=O absorption and a strongly intensified —OH band (which is shifted to slightly lower wavelengths); and in the spectrum of precipitate I, the dominant C=C absorption occurs at 6·37μ, instead of being located at 6·25μ as for the other two fractions. *Table 3* summarizes these changes; the extinctions listed in this table have been calculated by assuming the dominant band at (or near) 6·25μ to have the same intensity in all three cases and putting $E_{6\cdot25\mu} = 100$.

IV. THE INFRA-RED SPECTRA OF HUMIC ACID AND HUMATES

Humic acids and oxidized coals have been the subject of detailed investigation by M. Čeh and D. Hadži[11], G. Bergmann *et al.*[12] and others, and generally proved to be no more amenable to exploration by i.r. spectroscopy than the parent coals themselves. Since, however, there are still some divergencies of views between different investigators, it was thought useful to re-examine a few preparations. The specific objectives of the present determinations were (*a*) to ascertain what spectral changes other than the development of a strong C=O absorption band accompanied the oxidation of coal, and (*b*) to discover whether the position and intensity of the 6·2μ band are significantly affected by such oxidation. In particular, information was sought on whether, in the case of humates, this band was affected by the nature of the cation.

The humic acid was prepared by oxidizing finely ground Coal No. 2 in air at about 120°C, extracting the oxidized coal with aqueous alkali and finally precipitating humic acid with hydrochloric acid. Prior to spectroscopic examination, it was repeatedly washed with distilled water and carefully dried *in vacuo*. Salts of humic acid (humates) were prepared by stirring weighed

amounts of humic acid with the theoretically required quantities of potassium hydroxide, sodium hydroxide, etc. and evaporating the resultant solution to dryness. All i.r. spectra were determined on potassium bromide discs containing 0·2 per cent of sample.

The spectrum of the humic acid is reproduced in *Figure 9*. Compared with the spectrum of the parent coal (cf. *Figure 1*), it contains a much intensified

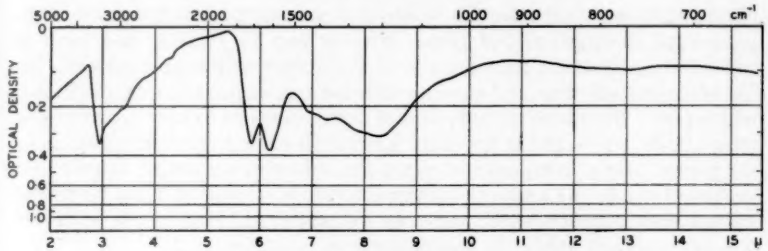


Figure 9. Infra-red spectrum of humic acid from Coal No. 2

—OH absorption band near 2·9μ, whose shape is similar to that of the 2·9μ band in the pyridine-extract spectrum; a very sharp, intense C=O band at 5·83μ; and broad absorption (due to carboxylic C—O) centring about 8·3μ. Significantly, *absorption due to non-aromatic* C—H (*at 3·45, 3·52, 6·85 and 7·25μ*) *is virtually eliminated.*

Infra-red absorption by humates (see *Figure 10*) at wavelengths below 5·5μ is identical with absorption by humic acid, and even the —OH band remains

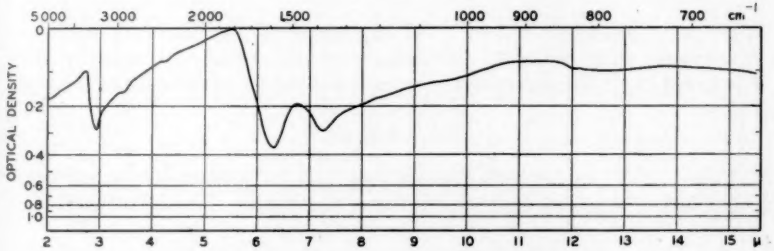


Figure 10. Infra-red spectrum of sodium humate from Coal No. 2

(surprisingly) unchanged. On the other hand, there is the inevitable modification of the absorption pattern at higher wavelengths; because of the neutralization the carbonyl band at 5·83μ is entirely eliminated, and C—O absorption around 8·3μ is replaced by a strong but somewhat ill-defined absorption around 7·25μ, assigned to symmetrical vibrations of the carboxyl ion. At the same time, the 6·2μ band is enhanced by asymmetrical vibrations of the carboxyl ion and occasionally significantly displaced. Examination of the spectra of the salts of potassium, sodium, magnesium, calcium, aluminium and iron indicated that this band can peak at any point between 6·20 and

6·40μ, but failed to establish any systematic variation of position with cation charge, radius or electronegativity[13]. Band-splitting, such as has recently been found by B. ELLIS and H. PYSZORA[14] with stearates, is either absent or masked by absorption due to C=C structures.

V. ON A PARTIAL RESOLUTION OF A PYRIDINE-EXTRACT OF COAL

Attempts to resolve coal extracts, especially pyridine-extracts, in order to obtain fractions more amenable to detailed characterization date back to the pioneering investigations of Bone, Wheeler and F. Fischer, and have at various times involved fractionation of the extract with simple solvents, the use of solvent mixtures, and more recently the application of chromatographic techniques[15]. But since only very limited success appears to have accompanied these efforts, a re-examination of the general problem is of some relevance. In the present study, attention was again focused upon a pyridine extract; but instead of employing a series of different solvents, resolution of the combined extract with pyridine–water mixtures was explored, *water being added in order variously to reduce the solvent power of pyridine*.

The experimental method consisted, then, in successively extracting the solid pyridine-extract (which had been prepared from Coal No. 2) with hot pyridine–water mixtures containing 20, 40, 60 and 80 per cent pyridine, regenerating each fraction, and finally submitting them to i.r. spectroscopy and x-ray diffraction. (The latter series of measurements was intended to offer information about possible differences in the sizes of the crystallites comprising each fraction.) From the diffraction patterns, the average crystallite height, i.e. the c dimension, was calculated by means of the Laue equation

$$c = k\lambda/(B \cos \theta)$$

where k = constant ($\sim$ 1·0), λ = wavelength of x-radiation (1·5402 Å), B = angular width of the 002 diffraction maximum at half-peak intensity, and θ = Bragg angle. The interplanar spacing d was computed from the expression

$$d = \lambda\, k/(2 \sin \theta)$$

From the i.r. spectra, absorbances (log I_0/I) for some major bands were calculated. The results of these calculations have been summarized in *Tables 4* and *5*.

Qualitatively, the i.r. spectra of the various fractions (cf. *Figure 11*) are as unpromising as the spectrum of the combined pyridine-extract: all spectra are again essentially coal-like, and none shows features not previously observed in the coal or extract spectra. Quantitatively, however, there is fairly clear evidence of partial separation. Thus, as the proportion of pyridine in the pyridine–water mixture used for the extraction increases, carbonyl absorption at 5·85μ tends to decrease and bands assigned to non-aromatic C—H intensify. (Absorption intensities of bands due to O—H at 2·9μ, C=C at 6·2μ and C—O at 7·80μ remain effectively unchanged*.)

* The fact that the C=O absorption at 5·85μ changes with the concentration of pyridine in the pyridine–water mixture, while the C—O absorption at 7·80μ does not, suggests that the two bands originate in different structures. Tentatively, we incline to the view that the 7·80μ band may be due to ether structures.

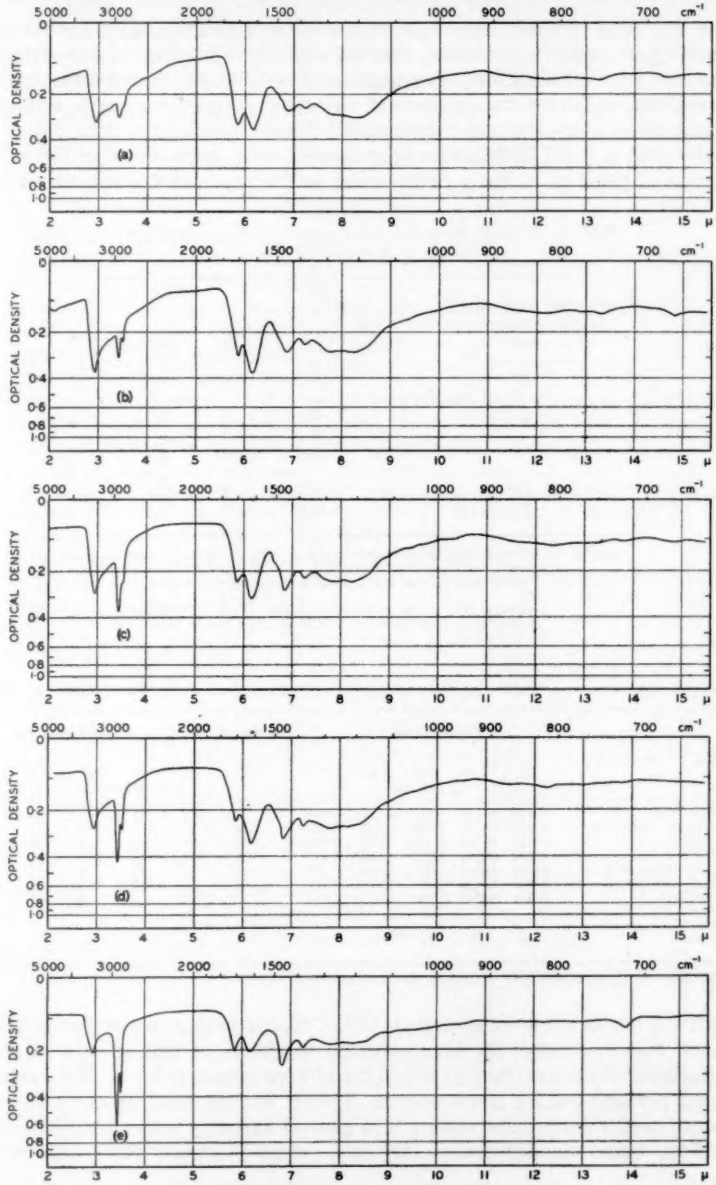


Figure. 11. Infra-red spectra of fractions of a pyridine-extract of Coal No. 2. Fraction soluble in (a) *20 pyridine–80 water,* (b) *40 pyridine–60 water,* (c) *60 pyridine–40 water,* (d) *80 pyridine–20 water, and* (e) *100 per cent pyridine*

In the light of these observations, the x-ray diffraction data set out in *Table 4* gain added significance. The 002 diffraction maxima of the various fractions were all markedly asymmetrical towards higher Bragg angles and, if resolved, indicated the presence of two main components, each with its characteristic d spacing and c dimension*. Since the second of these components (with $d = 4{\cdot}0$ Å) becomes progressively more pronounced as the proportion of pyridine in the pyridine–water mixture increases, it is possible to

Table 4. Average crystallite heights and interplanar spacings in fractions of a pyridine-extract

Pyridine in pyridine—water mixture, per cent		*d* Å	*c* Å	*Note*
20		5·1	11·4	*A*
40		5·1	11·8	*A*
	(*i*)	5·1	13·4	*B*
	(*ii*)	4·0	20·8	*B*
60	(*i*)	5·2	13·9	*B*
	(*ii*)	4·0	24·5	*B*

NOTES : Although the 002 diffraction peak was in all three instances strongly asymmetrical (see text),
A: denotes that it was *not* resolved for purposes of calculation, and
B: indicates that it was resolved, and that d and c were subsequently calculated for each of the two components designated by (*i*) and (*ii*).

Table 5. Absorption intensities in the i.r. spectra of fractions of a pyridine-extract of coal

λ, μ *Assignment*	*Absorbance*, log I_0/I					*Absorbance, per cent of absorbance of 6·20μ band*				
	20	40	60	80	*R**	20	40	60	80	*R**
			% *pyridine*					% *pyridine*		
2·93 —OH	0·238	0·329	0·273	0·240	0·148	92	113	99	96	128
3·45 C—H *stretching*	0·098	0·139	0·280	0·361	0·601	38	47	112	144	523
5·85 C=O	0·216	0·189	0·184	0·129	0·116	83	68	72	52	101
6·20 C=C	0·259	0·291	0·250	0·250	0·115	100	100	100	100	100
6·85 C—H *bending*	0·064	0·091	0·125	0·141	0·129	25	31	50	56	112
7·25 C—H (CH_2)	0·022	0·025	0·031	0·049	0·030	8·5	8·6	12·4	19·6	26·1
7·80 C—O—C	0·021	0·031	0·024	0·022	0·013	8·1	10·6	9·6	8·8	11·3
Yield, % of original extract	10	22	25	38	5					

* Residue of original extract after extraction with 80 pyridine–20 water.

associate it with the more saturated (CH_2/CH_3-rich) structures of the spectral series, and to connect the C=O-bearing structures of that series with the diffraction component having a spacing of approximately 5·1 Å. If the combined pyridine-extract is considered as more or less representative of the parent coal, the resultant picture is in general harmony with an earlier suggestion, based on differential thermal analysis studies[16], that coals may

* Whether the increase in the c dimension that accompanies the increase in the pyridine concentration in the solvent mixture is significant is uncertain. If real, it would suggest better stacking of layer-planes because of the previous more efficient removal of interfering material. However, for the time being, it will be wiser to regard the increase as part of an experimental error entailed in the resolution of the 002 reflection.

represent a series of clathrate compounds whose two components are closely related to lignin and cellulose. The *d* spacings found with the various pyridine-extract fractions would not be inconsistent with such a view.

Research Council of Alberta,
Edmonton, Alberta

(*Received October 1957*)

REFERENCES

[1] FRIEDEL, R. A. and QUEISER, J. A. *Analyt. Chem.* 28 (1956) 22
[2] BERGMANN, G., HUCK, G., KARWEIL, J. and LUTHER, H. *BrennstChemie* 35 (1954) 175
[3] BROWN, J. K. *J. chem. Soc.* (1955) 744
[4] GORDON, R. R., ADAMS, W. N. and JENKINS, G. I. *Nature, Lond.* 170 (1952) 317
[5] CANNON, C. G. *Nature, Lond.* 171 (1953) 308
[6] BROWN, J. K. *Nature, Lond.* 175 (1955) 229
[7] WYSS, W. F. *Chem. & Ind.* (1956) 1095
[8] VAN VUCHT, H. J., RIETVELD, B. J. and VAN KREVELEN, D. W. *Fuel, Lond.* 34 (1955) 50
[9] DRYDEN, I. G. C. *J. Inst. Fuel* 30 (1957) 193
[10] ADAMS, W. N. and PITT, G. J. Private communication.
[11] ČEH, M. and HADŽI, D. *Fuel, Lond.* 35 (1956) 77
[12] BERGMANN, G., HUCK, G., KARWEIL, J. and LUTHER, H. *Proceedings of the Second International Coal Conference, Valkenburg, 1957.* Cf. *BrennstChemie* 39 (1958) 520
[13] KAGARISE, R. E. *J. phys. Chem.* 59 (1955) 271
[14] ELLIS, B. and PYSZORA, H. *Nature, Lond.* 181 (1958) 181
[15] KIRKBY, W. A., LAKEY, J. R. A. and SARJANT, R. J. *Fuel, Lond.* 33 (1954) 480
[16] BERKOWITZ, N. *Fuel, Lond.* 36 (1957) 355

Optical Properties of Graphite and Coal

J. T. McCartney and S. Ergun

Determinations of indices of refraction and absorption of graphite and coal have been refined by a linear transformation of the Fresnel equation relating these parameters to microscopic measurements of reflectivity in air, water and cedar oil. This technique has been applied to single crystals of graphite, permitting for the first time the determination of these optical constants in directions parallel and perpendicular to the layer planes.

The optical constants of different coals have been determined in a similar manner, and their variation with metamorphism and approach to those of graphite have been studied. An approximate linear relationship has been found between log *reflectivity and hydrogen/carbon ratio, having the form* $R = R_e \exp[-\alpha(H/C)]$, *where* R_e *is the reflectivity of graphite and* α *is a constant, the slope of the line. A similar relation has been observed between absorption index and hydrogen/carbon ratio, whereas the variation of refractive index with metamorphism was small. The absorption index was found to be a sensitive criterion of structural variations in graphite and coal.*

The petrographic components of coal, when observed on polished surfaces by microscopic examination in reflected light, are classified according to their reflectivity and morphological nature. Quantitative measurements of reflectivity are usually not made in routine petrographic analysis, but such determinations have been made by various investigators, particularly on the major component of most banded coals, called anthraxylon or vitrinite[1–6]. These studies showed that the reflectivity of vitrinite increased rather regularly with increasing metamorphism or rank of the coal from lignite to anthracite. In fact, reflectivity has been proposed by some investigators as a measure of rank or degree of coalification.

Several of the workers[3, 6] measured the reflectivity of vitrinite in different media and, by means of a theoretical equation derived by Fresnel, calculated the indices of refraction and absorption. The equation is

$$r = \frac{R}{100} = \frac{(n - n_m)^2 + n^2k^2}{(n + n_m)^2 + n^2k^2}$$

where r is the fraction of vertically incident light reflected (R when expressed as per cent), n and k are the indices of refraction and absorption of the vitrinite, and n_m the refractive index of the medium used. The absorption index, k, is defined by an equation similar to Lambert's

$$I = I_0 \exp(-4\pi nkd/\lambda)$$

which represents the diminution of light intensity in passing through a thickness, d, of the material in question. J. Schuyer and D. W. van Krevelen[7] used the index of refraction and the related molar refraction in formulating a model of the molecular structure of coal. Thus the reflectivity and the indices of refraction and absorption of the optically different components of coal appear to be characteristic, conveniently measurable physical properties that should be valuable in the determination of fundamental differences in the

various coal components and in the problem of determining the basic molecular structure of coal.

Because most theories of coal structure assume that graphite is the end product of the coalification series, determination of its optical constants and their relation to those of high rank coal should be of value in the investigation of coal structure. Very little is known about the optical constants of graphite. A. N. WINCHELL[8], an authority on optical mineralogy, refers only to a study of 1923 which states that the average index of refraction of graphite lies between 1·93 and 2·07, and to two obscure references of about 1910 that give the index as about 3·0. H. SENFTLEBEN and E. BENEDICT[9] gave values of 1·96 and 0·34 for the average indices of refraction and absorption in green light. F. J. HUNTJENS and D. W. VAN KREVELEN[3] and B. C. MUKHERJEE[5] independently calculated from reflectivity measurements that the maximum index of refraction in green light is 2·00 to 2·02. No information appears to be available as to the magnitude of the optical anisotropy of graphite.

Coal has been found to be optically uniaxial with its optic axis perpendicular to the bedding planes[10] and to have maximum and minimum indices of refraction and absorption depending on the direction of polarization of the incident light with respect to the bedding. According to Winchell[8], graphite is also uniaxial. Its maximum indices may be obtained from reflectivity measurements on its common cleavage surfaces which are parallel to the layer planes. The minimum indices can be calculated from measurements on faces inclined to the basal planes, but these do not commonly occur in natural or artificial polycrystalline specimens. Single crystals are required that have plane faces inclined to the basal planes. Such crystals of graphite are rare and very small. However, probably the best collection in existence, that of the late Professor CHARLES PALACHE[11] of Harvard University, was loaned to the Bureau of Mines for these studies.

EXPERIMENTAL PROCEDURE

A diagram of the equipment used for reflectivity measurements is shown in *Figure 1*. Light that was kept at constant intensity by a battery-charging stabilizer was collected by a weakly diffusing lens, adjusted in intensity by an aperture diaphragm, filtered to pass only in the range from 5000 to 5700 Å with a maximum at 5500 Å, polarized by a Nicol prism, then led through a field diaphragm, and reflected by a prism through a microscope objective to the specimen surface. The reflected light then passed either to a side observation tube or directly to a photomultiplier cathode, through an adjustable aperture in the ocular. Reflectivity measurements were made in air, water and cedar oil with appropriately corrected objectives of about 60× magnification. An 8× ocular was used, producing an overall magnification of about 480×. For the measurements on relatively large homogeneous areas of vitrinite in coal, the ocular aperture restricted the effective area for reflectivity measurement to a circle of 43 microns diameter; clean, uniform areas on the natural faces of the graphite crystals were so small that a 5 micron aperture was used. Reflectivities in the various media were obtained by comparing the photomultiplier photometer readings with those obtained on standard mineral specimens of quartz, calcium tungstate or sphalerite.

Clean, fresh cleavage surfaces of graphite were obtained by peeling thin flakes from the natural basal surfaces of single crystals. This technique cannot be used on the faces inclined to the layer planes. These were cleaned as well as possible by washing in hydrochloric acid and distilled water. The crystals were set in plasticine and mounted on a Federov universal stage. The stage was adjusted by tilting in two directions until the desired surface

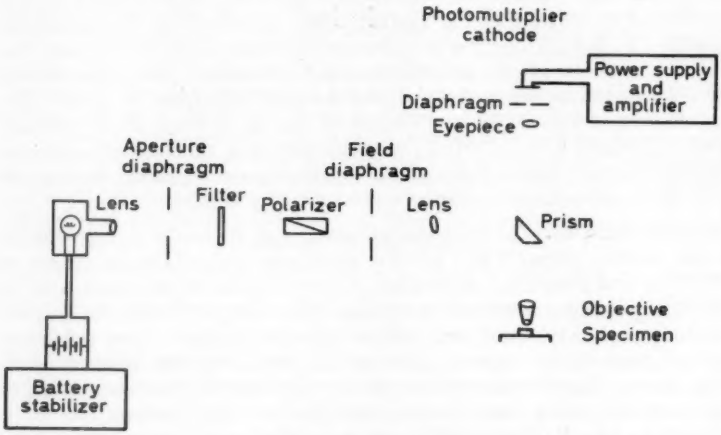


Figure 1. Schematic diagram of equipment for measuring coal reflectivity

was perpendicular to the microscope axis. Reflectivity measurements were made on the basal surfaces with no particular orientation to the plane of polarization of the incident light because the readings on a surface perpendicular to the optic axis are the same in any azimuth. With the inclined faces, the stage was rotated through 360° in the plane of the crystal face and two maximum and two minimum reflectivity readings were obtained. The maximum occurred when the polarized incident light vibrated parallel to the layer planes, and was comparable to that obtained on the basal faces. The minimum reflectivity was obtained with the layers perpendicular to the plane of polarization.

Figure 2 shows a sketch of a typical graphite crystal. The upper and lower portions are probably twin crystals produced by rotation and gliding on the 0001 planes. Most of the crystals were less than 1 mm in diameter and 0·5 mm in thickness. The most conveniently observed inclined faces were those making an angle of about 58° with the basal planes. These have been described by Palache[11] as the o or $10\bar{1}2$ faces. To calculate the minimum indices of refraction and absorption from reflectivity determinations on these faces, use was made of the uniaxial indicatrix, a three-dimensional geometric figure showing the variation of the indices of refraction of light waves in their directions of vibration. *Figure 2* also shows a principal section of a uniaxial negative indicatrix. OA is parallel to the basal plane and its length represents the maximum index of refraction. OB is proportional to the minimum

index. If OC is parallel to the crystal face being observed, light polarized parallel to the layer planes will vibrate perpendicular to the plane of the figure and have an index proportional to OA, while that polarized perpendicular to the layers will vibrate along OC and its index is proportional to OC. Thus from maximum and minimum reflectivity measurements on the crystal face making a known angle with the basal planes, points A and C can be located, and from the equation for the ellipse

$$x^2/a^2 + y^2/b^2 = 1$$

b, the length of the semi-minor axis and a measure of the minimum index of refraction of the crystal, may be calculated.

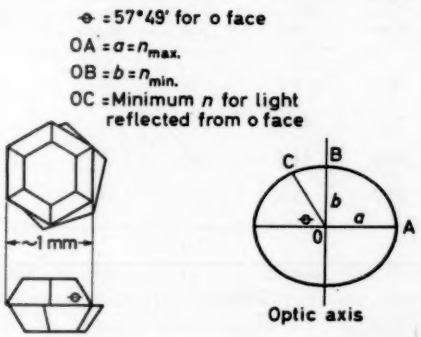


Figure 2. Sketch of a typical graphite crystal and diagram of a uniaxial indicatrix showing indices of refraction for light vibrating in various directions with the crystal axis

Uniform areas of the vitrinite component of coals were prepared by well-known polishing procedures. A face perpendicular to the bedding was roughly ground on silicon carbide laps, smoothed further on a fine Belgian hone, then given a final polish with wet alumina or magnesium oxide on microcloth. The polished face was mounted perpendicular to the microscope axis and the reflectivity measured with the light polarized parallel and perpendicular to the bedding planes.

RESULTS

The Fresnel equation

$$r = \frac{(n - n_m)^2 + n^2k^2}{(n + n_m)^2 + n^2k^2}$$

may be placed in a linear form by deriving an expression for

$$(1 + r)/(1 - r)$$

then writing the relation as follows

$$2n_m(1 + r)/(1 - r) = n(1 + k^2) + (1/n)(n_m)^2$$

This corresponds to the linear form, $y = a + bx$, where $a = n(1 + k^2)$

and $b = 1/n$. Reflectivity data for graphite are listed in *Table 1* and the resulting values of the functions for the linear equation are plotted in *Figure 3*. Readings in three media on two fresh basal surfaces and on o faces of two single crystals are shown. Also listed in *Table 1* are the calculated values of the refraction and absorption indices, with the probable errors of the mean for each.

Table 1. Reflectivity determinations on faces of graphite crystals and calculated indices of refraction and absorption

(Wavelength of light 5000 to 5700 Å; maximum at 5500 Å)

Face	Maximum reflectivity, per cent			Minimum reflectivity, per cent		
	Air	Water	Oil	Air	Water	Oil
Basal	27·7	18·9	15·1	—	—	—
Basal	28·0	19·2	16·1	—	—	—
o	26·5	18·9	14·5	13·2	5·5	3·1
o	27·5	18·0	15·1	11·3	4·2	2·3

Face	Indices			
	Refraction		Absorption	
	Maximum	Minimum	Maximum	Minimum
Basal	2·15 ±0·03	—	0·66 ±0·02	—
o	2·15 ±0·04	2·04* ±0·04	0·63 ±0·03	0·01*

* The minimum values of n and k, for light vibrating parallel to the optic axis, calculated from the minima on the o faces are 2·00 ±0·04 and 0·01, respectively.

The maximum reflectivity values for the o faces should be equivalent to those of the basal faces, but they are somewhat lower, probably because of the contrast in cleanliness and uniformity of the two surfaces. However, the calculated indices agree well. The reflectivities are appreciably higher than those reported by Huntjens and van Krevelen[3] and by Mukherjee[5]. The former gave maximum reflectivities of 22·1 and 11·0 per cent in air and oil, and the latter 22·2 and 11·1 per cent. A possible explanation might lie in the selection or preparation of the surfaces studied. No description of this was given by either of the above investigators. It is probable that the fresh basal surfaces used in this study were nearly perfect. The maximum indices of refraction and absorption are also about 7 per cent and 18 per cent higher, respectively, than those of the other two investigators.

The minimum index of refraction is not much lower than the maximum, contrary to what might be expected from the relatively large decrease in reflectivity. This characteristic is similar to that exhibited by coal. Huntjens and van Krevelen[3] noted that the index of refraction changes only slightly in high rank coals and the variations in reflectivity are caused almost entirely

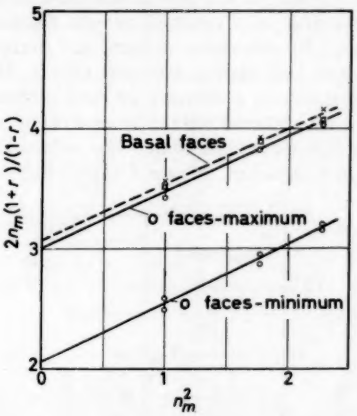


Figure 3. Variation of reflectivity function for basal and o faces of graphite crystals with refractive index of observational medium

by changes in absorptivity. It is obvious that this is so with graphite, because the minimum index of absorption is very much less than the maximum. Indeed, this value is surprisingly low. It is much less than the minimum absorption index of high rank coal (*Table 2*), being of the order of that for the lowest rank coal. Such a low value of k is usually associated with dielectrics

Table 2. Reflectivity determinations and calculated indices of refraction and absorption for the vitrinite (anthraxylon) component of coals of different rank

Coal bed	State	Rank*	H/C (atomic)	Reflectivity, per cent				Indices			
				∥ to bedding		⊥ to bedding		Refraction		Absorption	
				Air	Oil	Air	Oil	∥	⊥	∥	⊥
Hanna No. 2	*Wyo.*	*Suba*	0·909	7·5	0·56	7·3	0·51	1·75	1·74	0·03	0·04
Pittsburgh	*Pa*	*Hvab*	0·798	8·2	0·90	8·0	0·78	1·78	1·78	0·09	0·07
Chilton	*W. Va*	*Hvab*	0·778	8·6	0·95	8·3	0·81	1·82	1·81	0·06	0·02
Mary Lee	*Ala.*	*Mvb*	0·760	8·7	1·09	8·7	1·03	1·81	1·82	0·10	0·08
Beckley	*W. Va*	*Lvb*	0·650	9·8	1·58	9·6	1·39	1·87	1·87	0·12	0·09
'Alberta'	*Canada*	*Lvb*	0·617	10·1	1·71	9·5	1·41	1·89	1·86	0·13	0·11
Bernice	*Pa*	*Sa*	0·498	11·6	2·40	10·5	1·74	1·98	1·94	0·14	0·08
'Berkeley'	*W. Va*	*Sa*	—	11·9	2·63	10·8	1·97	1·98	1·94	0·16	0·12
Upper Five Ft (Enterprise Slope)	*Pa*	*An*	0·374	14·3	4·62	12·0	3·22	1·98	1·89	0·31	0·26
Hillman	*Pa*	*An*	0·358	14·3	4·63	12·0	3·30	1·98	1·88	0·31	0·27

* Abbreviations designate rank classifications as follows: Suba, sub-bituminous A; Hvab, high volatile A bituminous; Mvb, medium volatile bituminous; Lvb, low volatile bituminous; Sa, semi-anthracite; and An, anthracite.

or non-conductors, but, according to W. PRIMAK and L. H. FUCHS[12], the resistivity of graphite perpendicular to the layer planes, although about 100 times greater than that along the planes, is still much less than that of low rank coal or dielectrics.

An attempt was made to compare the experimental values of n and k with those calculated from the Drude free-electron theory of metals, as was done by L. G. SCHULZ[13] for several metals, but the equations appear to be inapplicable for values of k less than 0·86 when n is about 2. k for metals is of the order of 3·0 or greater.

The results of the reflectivity determinations on coal are summarized in *Table 2* and in a series of graphs showing the variation of reflectivity, refractive and absorptive indices, and anisotropy with the ratio of the atomic hydrogen and carbon contents (H/C). This ratio has been used by several investigators as a measure of rank increase and of structural change. These data were obtained only in air and oil because the water lens was not available when this work was done. The values for graphite are also plotted at the zero H/C abscissa. *Figure 4* shows the variation of maximum reflectivity in

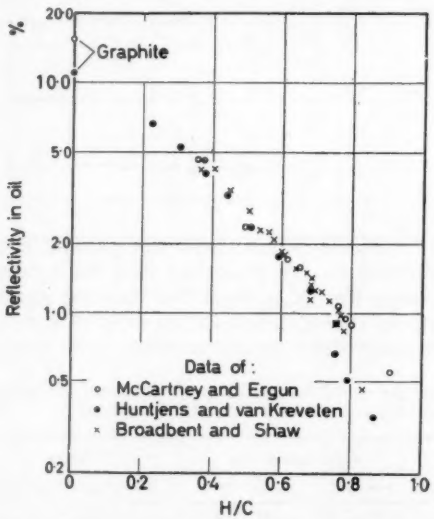


Figure 4. Variation of maximum reflectivity (in oil) of vitrinite (anthraxylon) in coal with hydrogen/carbon ratio

oil with H/C ratio. The reflectivities are plotted on a scale of logarithms. Also shown are results reported by Huntjens and van Krevelen[3] and by S. R. BROADBENT and A. J. SHAW[6]. In the former paper, data were given in a table as average values at different stages of coalification and probably reflect some smoothing of the individual fluctuations. The results of Broadbent and Shaw and of the present study are shown as individual determinations. The agreement among the three studies is good. The data approach a straight line over most of the range with some deviation at each end. This indicates an approximate relation of the form

$$R = R_g \exp\left[-\alpha(\mathrm{H/C})\right]$$

where R_g is the reflectivity of graphite, and α is a constant, i.e. the slope of the line. The experimental value of α in this study was found to be 3·6. The theoretical significance of α is not yet understood; therefore, the above

expression is empirical. It was observed that the reflectivity increases slowly with rank, i.e. with a decrease in H/C ratio, in the lower rank coals (H/C ratios greater than 0·7), then more rapidly in the higher ranks.

Figure 5 shows the variation of the maximum index of refraction of vitrinite in coal with H/C ratio. Also plotted on this graph are the results of C. G. CANNON and W. H. GEORGE[10], who measured the angle of maximum polarization (Brewster angle) rather than reflectivity. Their values are approximately

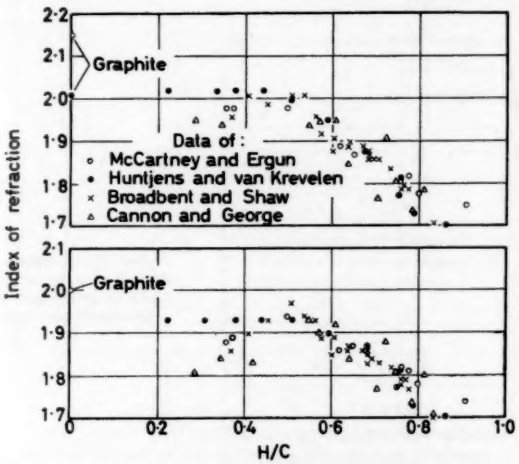


Figure 5. Variation of maximum (above) and minimum (below) index of refraction of vitrinite (anthraxylon) in coal with hydrogen/carbon ratio

corrected for difference in wavelength of light used according to dispersion curves given in their paper. These values agree fairly well with the results by reflectivity measurements, indicating that the two methods give values that are reasonably close to the true indices. The results of Cannon and George are probably too low for the highest rank coals because the method neglects the effects of absorption, which is high for these coals. The index of refraction tends to approach different constant values in each set. The maximum index of graphite found by Huntjens and van Krevelen[3] is about the same as the maximum for coal, but that of the present study is higher.

Also in *Figure 5* are plotted the minimum indices of refraction calculated from the reflectivity values at right angles to the bedding. An interesting feature of these data is an apparent decrease in index of the highest rank anthracites (H/C ratios less than 0·5). This is indicated by the values of three of the studies but not by those of Huntjens and van Krevelen. This may be related to the results of P. B. HIRSCH[14] who found that an X-ray scattering maximum at 20 Å became more diffuse for high rank anthracite, and he attributed it to increased local parallelism of the layers, with formation of groups of widely different numbers of layers packed at various distances.

Figure 6 shows the variation of maximum index of absorption with H/C ratio. These data also approach a logarithmic straight line relationship, but not as closely as the reflectance data of *Figure 4*. The maximum absorptive index of graphite logically concludes this trend. In general, the results of Broadbent and Shaw and of this study are higher than those of Huntjens and van Krevelen.

The absorption indices found by Cannon and George from measurements of the angles of principal incidence and azimuth are appreciably higher than

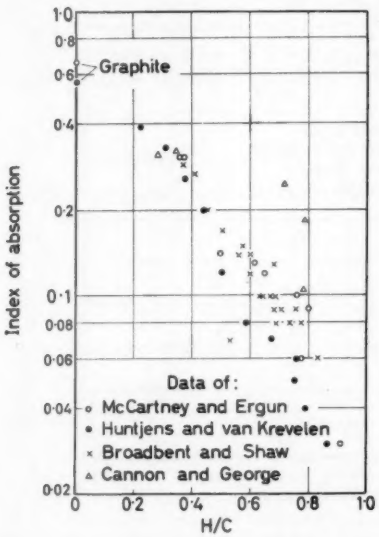


Figure 6. Variation of maximum index of absorption of vitrinite (anthraxylon) in coal with hydrogen/carbon ratio

the others for the medium rank coals. The differences may be due to the fact that their method gives only approximate results.

The minimum indices of absorption of coals also increase similarly to the maxima, but the minimum for graphite is so low that it indicates there is still a considerable difference in inter-layer structure between anthracite and graphite. Because the absorption index appears to be a much more sensitive criterion of structural variations in graphite and coal than the refractive index, direct determination of absorptivity in different coals and coal components should be advantageous. Measurement of the attenuation of light of different wavelengths in the vari-coloured components revealed in thin sections should provide significant data for determination of structural differences.

Figure 7 shows the relation to rank of anisotropy of vitrinites as measured by the ratio of minimum to maximum reflectivities in oil. Huntjens and van Krevelen show anisotropy beginning at an H/C ratio of about 0·75 (82 per cent carbon). Broadbent and Shaw and this study show some anisotropy in all ranks of coal and Hirsch's x-ray results also show evidence of ordering in all

coals examined. E. WEGE[4] emphasized that increase in anisotropy with rank is only a general trend and that there may be considerable variation within small rank changes depending on local pressure influences. The reflection anisotropy of graphite, largely affected by differences in maximum and minimum absorptivity, is considerably greater than that of high rank coal.

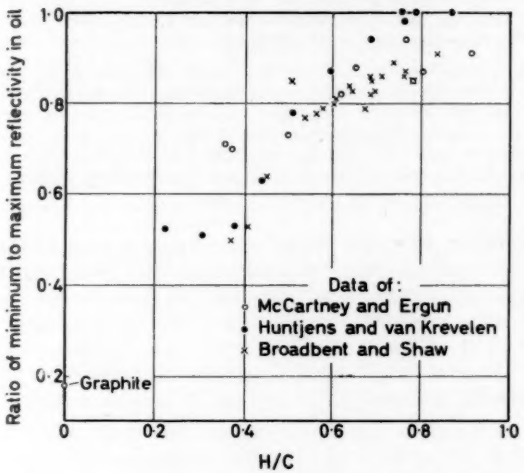


Figure 7. Relation to rank of the anisotropy of vitrinite (anthraxylon) in coal as measured by the ratio of minimum to maximum reflectivities in oil

The authors wish to acknowledge the assistance of W. E. Edmunds, formerly geologist, Bureau of Mines, who made many of the reflectivity determinations on coal. They are also grateful to Clifford Frondel, Professor of Mineralogy, Harvard University, who kindly made available the entire graphite crystal collection of the late Professor Charles Palache. Figures 1 to 7 are reproduced by courtesy of the U.S. Bureau of Mines.

Special Coal Research Section,
Bureau of Mines,
U.S. Dept of the Interior,
Pittsburgh 13, Pa

(*Received December 1957*)

REFERENCES

[1] HOFFMAN, E. and JENKNER, A. *Glückauf* 68 (1932) 81
HOFFMAN, E. and JENKNER, A. *Fuel, Lond.* 12 (1933) 98
[2] SEYLER, C. A. *Fuel, Lond.* 31 (1952) 159
[3] HUNTJENS, F. J. and VAN KREVELEN, D. W. *Fuel, Lond.* 33 (1954) 88
[4] WEGE, E. *BrennstChemie* 35 (1954) 1 and 35
[5] MUKHERJEE, B. C. *Fuel, Lond.* 31 (1952) 153
[6] BROADBENT, S. R. and SHAW, A. J. *Fuel, Lond.* 34 (1955) 385

[7] SCHUYER, J. and VAN KREVELEN, D. W. *Fuel, Lond.* 33 (1954) 176
[8] WINCHELL, A. N. *Elements of Optical Mineralogy*, Part II, p 14. Wiley: New York, 1933
[9] SENFTLEBEN, H. and BENEDICT, E. *Ann. Phys., Lpz.* 54 (1917) 65
SENFTLEBEN, H. and BENEDICT, E. *Int. crit. Tab.* 5 (1929) 249
[10] CANNON, C. G. and GEORGE, W. H. *Proc. Conf. Ultrafine Structure of Coals and Cokes*, p 290. British Coal Utilisation Research Association: London, 1944
[11] PALACHE, C. *Amer. Min.* 26 (1941) 709
[12] PRIMAK, W. and FUCHS, L. H. *Phys. Rev.* 95 (1954) 22
[13] SCHULZ, L. G. *J. opt. Soc. Amer.* 44 (1954) 540 and 47 (1957) 64
[14] HIRSCH, P. B. *Proc. Roy. Soc. A* 226 (1954) 143

The Mode of Occurrence of Chlorine in Coal

G. N. DAYBELL and W. J. S. PRINGLE

Work is described which establishes that a substantial part of the chlorine in coals from the central British coalfields is present as chloride ions attached to the coal substance by a linkage with ion exchange properties. Calcium and magnesium chlorides which appear in water extracts of coals are shown to be formed by reaction between the carbonate minerals present and hydrochloric acid produced from this ionic chlorine. The coals examined contained water-soluble sodium equivalent to from a third to a half of the total chlorine content.

VARIOUS opinions have been expressed as to the mode of combination of chlorine in British coals. Early investigators[1–3] reported that only part of the chlorine could be removed by extraction with water and suggested that some of it is chemically combined with the coal substance, either as organic chlorine or as adsorbed ions. Later workers, notably H. E. CROSSLEY[4], concluded that virtually the whole of the chlorine is present as alkali chlorides, possibly with small quantities of calcium and magnesium chlorides as well.

Until recently this latter view was widely accepted, but a reassessment of the position has been made necessary by the recent findings of L. J. EDGCOMBE[5]. He examined a series of twenty nine coals and found that, although all the chlorine could be extracted if the coal was sufficiently finely ground, the alkali in the extracts was equivalent to only part of the total chlorine, and hence that only part of the chlorine can be present as alkali chlorides. More than half the chlorine could be driven off from most of the coals by heating to 200°C in air, and he described experiments to demonstrate that the chlorine so evolved was not produced by the decomposition of alkali chlorides. He postulated that the volatile chlorine represents that part of the total chlorine which is not present as alkali chlorides and suggested that it exists in the coal as chloride ions held on the coal substance by ion exchange linkage.

The present work has been directed to a re-examination of the mode of combination of the chlorine in the coals of the Midlands Divisions of the National Coal Board, with particular reference to these recent findings of Edgcombe. It was carried out on a series of eighteen samples selected from those coalfields. Details of the samples are given in the Appendix.

EXTRACTION OF COAL WITH WATER

Experimental

The procedure adopted was to grind the samples in a laboratory ball mill for 24 hours and to boil 5 g of the milled samples with 200 ml water under reflux for 1·5 hours. In each case only one extraction was made.

In the examination of the extracts, calcium, magnesium, aluminium, iron, titanium, and phosphate were determined by the colorimetric methods

described by W. J. S. PRINGLE[6]. Soluble silica was determined by the colorimetric method of J. B. MULLIN and J. P. RILEY[7]. Sodium and potassium were determined by flame photometry using the EEL flame photometer. Sulphate was determined gravimetrically and chloride by the Volhard method. Blank determinations were made in all cases.

Preliminary experiments on four samples confirmed that very fine grinding is essential for complete extraction: *Table 1* shows that samples ground only to pass 240 B.S. mesh sieve retain part of their chlorine even after extraction with boiling water for 5 hours.

Table 1. Water solubility of chlorine—effect of particle size

Coal No.	% Chlorine (dry coal basis)			
	Total in coal	In water extract		
		Sample ground to pass 240 B.S. sieve		Sample ground in ball mill for 24 h
		Extracted for 1·5 h	Extracted for 5 h	Extracted for 1·5 h
—	1·02	0·85	0·92	1·01
1	0·63	0·50	0·56	0·61
2	0·48	0·44	0·46	0·49
6	0·52	0·33	0·37	0·50

Further preliminary work established that the increase in chlorine solubility with prolonged grinding is a simple particle size effect and is not due to an oxidation change rendering soluble that part of the chlorine which, in unoxidized coal, is insoluble. A coal of high chlorine content (1·03 per cent) was crushed to pass a 14 B.S. mesh sieve in a hand pestle and mortar and divided into two samples; one of the samples was ground in the ball mill for 24 hours in the usual way and the other was similarly ground in an atmosphere of nitrogen. In both cases the whole of the chlorine was extractable with boiling water in 1·5 hours.

Results

Table 2 summarizes the results of the examination of the water extracts of the selected coals.

As far as the relationship between water-soluble alkali and total chlorine was concerned, all the coals gave similar results: the chlorine equivalent of the soluble alkali ranged from 30 per cent to 54 per cent, in good agreement with the findings of Edgcombe. In other respects, however, the results from the first six coals, which had normal or high carbonate contents, differed from those of the remaining twelve, which had low carbonate contents. The main differences were:

(*1*) The extracts from the first six coals were neutral whereas those from the remaining twelve were acidic

Table 2. Analysis of water extracts

Coal No.	Analysis of coal (dry basis, per cent)			Analysis of extract (percentage on dry coal basis)								Chlorine extracted (% of total)	Total anions in extract (milli-equiv.)	Total metal cations in extract (milli-equiv.)	pH of extract	Chlorine equiv. of water-soluble sodium, as % of total chlorine
	Chlorine	Carbon dioxide	Sodium	Chlorine	Sulphate	Silicate	Sodium	Potassium	Calcium	Magnesium	Iron					
1	0·63	1·57	—	0·61	0·03	0·03	0·16	<0·01	0·18	0·05	•	97	18·6	20·0	7·0	40
2	0·48	0·26	0·16	0·49	<0·01	0·02	0·16	<0·01	0·15	0·01	•	100	14·4	14·8	6·5	50
3	1·03	0·71	—	1·01	—	—	—	—	—	—	—	98	—	—	—	—
4	0·81	1·54	—	0·81	—	—	—	—	—	—	—	100	—	—	—	—
5	0·15	1·04	—	0·14	—	—	—	—	—	—	—	94	—	—	—	—
6	0·52	0·47	0·13	0·50	0·03	0·02	0·13	<0·01	0·15	0·03	•	96	15·3	15·7	7·0	38
6A	0·56	0·04	0·18	0·43	<0·01	0·02	0·17	<0·01	0·02	0·01	0·01	77	12·8	9·2	4·0	46
7	0·72	0·05	0·26	0·58	<0·01	0·03	0·25	<0·01	0·04	0·01	0·01	81	17·1	14·1	4·0	54
8	0·51	0·10	0·17	0·43	<0·01	0·01	0·17	<0·01	0·05	0·01	0·02	84	12·4	10·8	5·0	51
9	0·64	0·08	0·20	0·52	<0·01	0·03	0·20	<0·01	0·07	0·01	0·01	81	15·5	13·1	4·5	47
10	1·02	0·04	0·28	0·71	<0·01	<0·01	0·27	<0·01	0·05	<0·01	<0·01	70	20·2	15·1	3·5	41
11	0·69	0·01	—	0·60	0·02	0·01	0·17	<0·01	0·03	<0·01	0·05	87	18·1	10·6	3·5	38
12	0·72	0·07	—	0·63	<0·01	0·02	0·16	<0·01	0·05	<0·01	0·02	88	19·0	10·5	3·5	35
13	0·72	0·09	—	0·66	0·09	0·03	0·22	0·01	0·14	0·01	0·03	91	22·0	19·0	4·0	47
14	0·83	0·03	—	0·73	—	—	—	—	—	—	—	88	—	—	—	—
15	1·05	0·04	—	0·83	<0·01	0·03	0·29	0·01	0·07	0·01	0·02	79	24·8	18·3	3·5	43
16	0·63	0·07	—	0·47	0·10	<0·01	0·12	<0·01	0·04	0·01	0·05	75	15·4	10·0	—	30
17	0·51	0·07	—	0·43	—	—	—	—	—	—	—	84	—	—	—	—

* Extract contained less than 0·002 per cent iron.

Determinations of aluminium and titanium were made on some of the extracts, but only traces of them were found.

(*2*) The extracts from the first six coals contained appreciable amounts of calcium and no iron whereas those from the remaining twelve contained very little calcium and significant amounts of iron

(*3*) Chlorine was completely extracted from the first six coals but only partly extracted from the remaining twelve.

The principal cation in all the extracts was chloride. The acidity of the extracts from the coals of low carbonate content and the appreciable excess of anions over metal cations in those extracts strongly indicate the presence of free hydrochloric acid. Edgcombe suggested that hydrochloric acid is a first product during water extraction and postulates that it is produced either by hydrolysis of organic chlorine compounds or from chlorine ions adsorbed on the coal acting as an ion exchange medium; the data above provide strong support for this view. His further suggestions, that the acid so produced reacts with the carbonates to form soluble calcium and magnesium chlorides and that the presence of calcium and magnesium in the extracts is due to that reaction rather than to the presence of naturally occurring calcium and magnesium chloride in coal, are also consistent with the present findings.

The behaviour of the iron provides further confirmation of the role of carbonates. Ferrous carbonate is a normal component of the carbonate minerals of British coals, and on aqueous extraction of coal the formation of ferrous chloride by reaction between the carbonate and the hydrochloric acid would be expected. In neutral extracts, such as those from coals of normal carbonate contents, ferrous chloride would be hydrolysed and no soluble iron would appear in the extracts. In acid extracts, however, hydrolysis of ferrous chloride does not occur and one would expect to find iron in solution, as one does in the extracts from coals of low carbonate content.

The general low level of calcium and magnesium in the extracts from the coals of low carbonate content, as compared with that in the extracts from the coals of high carbonate content, is strong presumptive evidence that these metals in the extract are derived from the respective carbonates, and in this connection the data relating to Coals 6 and 6A are important. These coals were samples from the same source, and the only substantial difference between them was that all visible ankerite was removed from Coal 6A by hand picking before milling. This removal of ankerite had little effect on the chlorine content, but reduced the amount of water-soluble calcium from 0·15 per cent to 0·02 per cent and of water-soluble magnesium from 0·03 per cent to 0·01 per cent. Had it been possible to remove the ankerite entirely, the amounts of water-soluble calcium and magnesium would probably have been still smaller.

One further major observation from these experiments is that chlorine is not completely extracted from coals of low carbonate content by the procedure adopted, although it is completely extracted from coals of normal or high carbonate content by that procedure. That this difference is a function of the carbonate content was confirmed by two additional sets of experiments. In the first set, extraction of a number of the coals of low carbonate content was repeated in the presence of added carbonate, 0·2 g of powdered calcium

carbonate (AnalaR) being added to the 5 g of coal to be extracted. The results are given in *Table 3.*

The effect of the addition of calcium carbonate is thus to bring into solution almost all of the chlorine not extracted by water alone under the conditions used. For the two coals of highest chlorine content (Coals 10

Table 3. Effect of added carbonate on the solubility of chlorine in coals of low carbonate content

Coal No.	*Carbon dioxide of coal (%, dry basis)*	*Chlorine of coal (%, dry basis)*	*Chlorine in extracts (%, dry coal basis)*	
			In extract of coal alone	*In extract of coal with added carbonate*
7	0·05	0·72	0·58	0·71
8	0·10	0·51	0·43	0·50
10	0·04	1·02	0·71	0·97
11	0·01	0·69	0·60	0·69
12	0·07	0·72	0·63	0·72
13	0·09	0·72	0·66	0·72
15	0·03	1·05	0·83	0·98

and 15) solution was still not quite complete; it appears that a considerable excess of carbonate over the chemical equivalent of the chlorine is necessary.

The second experiments were into the effect of removing carbonates from coals from which all the chlorine is normally soluble. One of the experiments involved hand picking of ankerite from Coal 6 and has been mentioned above: virtually all of the chlorine (0·52 per cent) from this coal was extractable with water, but when the visible ankerite was picked out prior to extraction (Coal 6A) only 0·43 per cent of chlorine could be extracted. The other experiment involved the removal of ankerite from two coals by digestion with cold 0·1N sulphuric acid for four hours, followed by extraction of the treated coals, and the effect on the solubility of the chlorine was the same as in the previous experiment.

Summing up, the work on extraction of coal with water has confirmed that only part of the chlorine in coal is associated with sodium and potassium and that the remainder is present not as metal chlorides but in a form which is fairly readily hydrolysed by boiling water to free hydrochloric acid. It has also been demonstrated that, with coals of very low carbonate content, extraction of chlorine by water is incomplete under conditions which suffice to extract completely the chlorine from coals of normal carbonate content.

EXTRACTION OF COAL WITH AQUEOUS SOLUTIONS

If that part of the chlorine which is not associated with alkalis exists as chloride ions attached to the coal substance by an ion exchange type of linkage, as suggested by Edgcombe, these ions should be replaceable by other anions. This can be investigated by extracting with suitable solutions those coals in which part of the chlorine is not extractable with water by the

extraction procedure adopted—if anion replacement occurs, the whole of the chlorine should go into solution. *Table 4* summarizes results obtained from one coal by this approach. The coal of low carbonate content (0·06 per cent) was boiled under reflux for one hour in a solution containing various anions.

It is apparent that both the nitrate and the hydroxyl ions are completely effective in bringing about solution of the chlorine and that sulphate ions are

Table 4. Extraction of a coal with various aqueous solutions (Chlorine content of coal: 0·60 per cent, dry coal basis)

Reagent	*Concentration*	*Chlorine in extract (%, dry coal basis)*
Water	—	0·36
Nitric acid	0·25%	0·57
Nitric acid	0·5%	0·58
Nitric acid	1·0%	0·59
Potassium nitrate	0·2%	0·57
Ammonium nitrate	0·2%	0·57
Zinc nitrate	0·19%	0·57
Sulphuric acid	0·1N	0·41
Sodium sulphate	1·0%	0·49
Magnesium sulphate	1·0%	0·48
Ferrous sulphate	0·2%	0·42
Ferric sulphate	0·2%	0·43
Sodium hydroxide	0·01N	0·60
Lithium hydroxide	0·04%	0·59

slightly more effective than water alone. This was confirmed by a more extended investigation involving a number of coals of low carbonate content (see *Table 5*).

These results are consistent with the type of linkage postulated. Following the statement of O. SAMUELSON[8] that the active groups in anion exchangers are amino and quaternary ammonium groups, it would be feasible to suppose

Table 5. Extraction of coals of low carbonate content with solutions containing various anions

Coal No.	*Chlorine in coal, per cent (dry coal basis)*	*Carbon dioxide in coal, per cent (dry coal basis)*	*Chlorine in extract, per cent, dry coal basis*				
			Water	*Potassium nitrate*		*Ammonium hydroxide*	*Sulphuric acid*
				0·1%	1·0%	0·1%	0·1N
6A	0·56	0·04	0·43	0·53	0·55	0·54	0·49
7	0·72	0·05	0·58	0·69	—	0·69	0·64
8	0·51	0·10	0·43	0·48	—	0·49	0·43
9	0·64	0·08	0·52	0·60	—	0·61	0·55
11	0·69	0·01	0·60	0·65	0·70	0·66	0·61
12	0·72	0·07	0·63	0·69	0·72	0·71	0·67
13	0·72	0·09	0·66	0·70	0·72	0·71	0·65
14	0·83	0·03	0·73	0·82	—	0·85	0·80
15	1·05	0·04	0·83	0·97	1·01	1·01	0·92
17	0·51	0·07	0·43	0·49	—	0·50	0·43

that the chloride ions are attached to an amino group in coal. Such a group peripheral to the condensed aromatic portion of the coal molecule might be expected to break away at an early stage of pyrolysis, and it is of great interest to recall H. TER MEULEN'S[1] observation of the formation of a sublimate of ammonium chloride in a tube in which a coal of high chlorine content was being heated in the presence of air.

On this hypothesis, the role of carbonates in promoting complete extraction of chlorine from coals in water becomes explicable. It is probable that the hydroxyl ion produced by the dissociation of water tends to replace the chlorine ions and that the carbonates, by removing excess hydrogen ions, allow the replacement to proceed to completion; in the absence of carbonates, replacement would effectively cease when an appreciable acid concentration had developed.

EFFECT OF HEATING ON CHLORINE IN COAL

Edgcombe found that a very substantial part of the chlorine can be removed as hydrochloric acid by heating coal in dry air for 24 hours, although none is removed by heating in the same way in nitrogen. He also described experiments which indicated that alkali and calcium chlorides do not lose chlorine when heated at 200°C with coal, and suggested that the volatile chlorine represents that part of the total chlorine which is held by ion exchange linkage.

These results have not been entirely confirmed by the present work. Four coals have been heated in air under the conditions described by Edgcombe, then ground in the ball mill and extracted with both water and nitrate solution. The unheated coals were similarly extracted. *Table 6* gives details of the chlorine lost by these coals during the heating process, and *Table 7* gives the analyses of the water extracts of both the heated and unheated coals.

Table 6. Loss of chlorine on heating coals at 200°C in air
(Results as per cent on dry coal basis)

Description	*Coal 6A*	*Coal 7*	*Coal 8*	*Coal 10*
Chlorine in unheated coal	0·56	0·72	0·51	1·02
Chlorine remaining in coal after heating	0·13	0·20	0·16	0·29
Chlorine lost on heating	0·43	0·52	0·35	0·73
Chlorine equivalent of soluble sodium	0·26	0·39	0·26	0·42

Although much of the chlorine is evolved on heating, that which remains in the coal is less than the equivalent of the soluble alkali, and much of the soluble sodium in the heated coal is presumably present as sulphate. Furthermore, only a fraction of the chlorine remaining in the heated coal is soluble on water extraction and no more of it can be extracted by nitrate solution than by water. The insolubility of the chlorine remaining in the coal after heating is probably due to a secondary reaction between the hydrochloric acid produced and the coal. L. HORTON[9] has stated that when coal is treated with dry hydrochloric acid gas at 100°C part of the chlorine absorbed is

insoluble in water. We have confirmed this work and have found that the water-insoluble absorbed chlorine is also insoluble in nitrate solutions.

These data indicate that decomposition of sodium chloride can occur under the conditions used. This indicated instability was proved by a direct experiment in which a coal of low chlorine content was allowed to stand in a solution

Table 7. Analysis of extracts from heated coals
(Results as per cent on dry coal basis)

Constituent	Coal 6A		Coal 7		Coal 8		Coal 10	
	Unheated coal	Heated coal	Unheated coal	Heated coal	Unheated coal	Heated coal	Unheated coal	Heated coal
Sodium (in water extract)	0·17	0·16	0·25	0·23	0·17	0·15	0·27	0·24
Calcium (in water extract)	0·02	0·01	0·04	0·01	0·05	0·02	0·05	0·02
Chloride (in water extract)	0·43	0·04	0·58	0·09	0·43	0·06	0·71	0·07
Sulphate (in water extract)	<0·01	0·34	<0·01	0·28	<0·01	0·18	<0·01	0·40
Silicate (in water extract)	0·02	0·02	0·03	0·02	0·01	0·01	<0·01	<0·01
Chloride in extract with nitrate solution	0·55	0·03	0·69	0·10	0·48	0·04	1·00	0·06
Total chlorine in coal	0·56	0·13	0·72	0·20	0·53	0·16	1·02	0·29

NOTE: The extracts of the heated coals were examined for potassium, magnesium and iron but only traces were found.

of sodium chloride for some time, then dried at 70°C and heated in dry air at 200°C for 24 hours.

The decomposition is possibly the result of chemical interaction of sodium chloride with some compound present in the coal or formed during the heating process; the compound responsible could well be the sulphate formed by oxidation of pyrites or organic sulphur, but this has not been further

Table 8. Heating of coal treated with sodium chloride solution
(Results as per cent on dry coal basis)

Description	Untreated coal	Coal treated with sodium chloride solution	Treated coal after heating
Total chloride in coal	0·02	1·01	0·52
Chlorine in water extract	0·02	1·02	—

investigated. It is also possible, however, that when sodium chloride is added in solution, chloride ions become adsorbed on the coal and behave in the same way on heating as the chlorine naturally present.

Whatever the cause of the decomposition, the fact that it occurs makes untenable the theory that the volatile chloride is derived solely from that part of the chlorine which is not present as alkali chorides.

Two further experiments were carried out on the effect of heating at 200°C for 24 hours in a variety of other atmospheres. Two coals were used and the results are given in *Table 9*.

Significant amounts of chlorine were evolved from the two coals when heated in nitrogen, even when the last traces of oxygen were removed. Under these conditions, oxidation cannot be the agency responsible for chloride

Table 9. Chlorine evolved on heating coals at 200°C in various atmospheres

Atmosphere	*Coal 4 (total chlorine 0·81%)*		*Coal 16 (total chlorine 0·63%)*	
	Chlorine evolved on heating (per cent, dry coal basis)	*Chlorine evolved as % of total chlorine*	*Chlorine evolved on heating (per cent, dry coal basis)*	*Chlorine evolved as % of total chlorine*
Dry air	0·53	66	0·47	75
Moist air	0·60	74	0·52	83
Dry nitrogen	0·26	32	0·33	52
Moist nitrogen	0·33	41	—	—
Dry oxygen-free nitrogen, with coal dried in vacuum desiccator before use	0·29	36	—	—

decomposition and the decomposition would appear to be a direct result of pyrolysis or of hydrolysis by water derived from the water of constitution of shale. Evolution of hydrochloric acid on heating in the absence of oxygen was also found by C. W. YEARSLEY[2] who showed that 70 per cent of the chlorine could be driven off by boiling coal in tetralin (b.pt 206°C).

CONCLUSIONS AND DISCUSSION

It has been confirmed that when coals containing normal amounts of carbonate minerals (i.e. 0·25 to 1·5 per cent) are finely ground, the whole of the chlorine in them is soluble in boiling water. From studies of the aqueous extracts it has also been confirmed that only part of the chlorine in coal can be present as sodium chloride and that potassium, calcium and magnesium chlorides are not present in significant amounts. With coals containing very small amounts of carbonates (i.e. 0·1 per cent or less), extraction of chlorine by water is incomplete under conditions which suffice to extract completely the chlorine from coals of normal chlorine content, and it has been established that the carbonates in coal have a function in the solution of chlorine. The results of experiments on extracting chlorine in a variety of reagents are consistent with the view that part of the chlorine exists as chloride ions held on the coal substance by ion exchange linkage and it has been demonstrated that these ions can be replaced by other anions. Edgcombe's finding that much of the chlorine in coal can be driven off as hydrochloric acid on heating in air at 200°C has been substantiated, but the hypothesis that this volatile chlorine could not in part result from decomposition of sodium chloride has not been confirmed. It has been shown that sodium chloride in intimate contact with coal undergoes decomposition when heated under the conditions described, and that much of the chloride remaining in the coal after heating is in a form not originally present in the coal.

The practical field in which the question of the nature of chlorine in coal is of major interest is that of steam raising, particularly for power generation. There is no doubt that combustion of high-chlorine coal in boilers results in serious fouling by alkali-bonded deposits[10]. Although the work described in this paper clearly shows that the relationship of chlorine to alkali is not stoichiometric, the analytical data in the paper demonstrate that high chlorine content is generally associated with high alkali content, and the common practice of regarding the amount of chlorine in coal as a guide to the measure of alkali content remains a reasonable working rule when facilities for alkali determination are not available.

This investigation has been carried out at the Birmingham and Nottingham Coal Survey Laboratories as part of the programme of the Coal Survey Branch of the Scientific Department of the National Coal Board. The authors acknowledge, with thanks, permission to publish the results.

National Coal Board,
Albert Embankment,
London, S.E. 11.

(*Received November 1957*)

Appendix. Details of coals used

Coal No.	Coalfield	Colliery or borehole	Seam	% air-dried coal				Coal Rank Code
				Moisture	Ash	Chlorine	Carbon dioxide	
1	Notts. and N. Derbys.	Moorgreen	Tupton	9·7	3·5	0·57	1·42	702
2	Notts. and N. Derbys.	Mansfield	High Hazel	7·0	3·2	0·46	0·24	802
3	Notts. and N. Derbys.	Thoresby	Top Hard	7·5	3·7	0·95	0·66	802
4	Cannock	Littleton No. 2	Top Robins	8·7	8·6	0·74	1·41	802
5	Warwick	Binley	Nine Feet	10·4	6·6	0·13	0·93	902
6	Notts. and N. Derbys.	Shirebrook	Clowne	6·0	3·3	0·48	0·43	802
6A				6·0	3·2	0·51	0·04	
7	Notts. and N. Derbys.	Rufford	Top Hard	5·2	4·5	0·68	0·05	801
8	Notts. and N. Derbys.	Sherwood	Dunsil	5·7	2·0	0·48	0·09	802
9	Notts. and N. Derbys.	Blidworth	Top Hard	4·9	4·9	0·60	0·07	702
10	Notts. and N. Derbys.	Thoresby	Top Hard	9·1	1·7	0·94	0·04	802
11	Cannock	Lea Hall	Unidentified	11·7	4·2	0·61	0·01	802
12	Shropshire	Alveley No. 4 B/H	Flying Reed	10·9	2·4	0·64	0·06	802
13	Cannock	Calf Heath B/H	Eight Feet	9·4	3·8	0·66	0·08	802
14	Cannock	Calf Heath B/H	Seam at 1769 ft	7·5	16·3	0·77	0·03	802
15	Cannock	Calf Heath B/H	Mealey Greys	7·8	5·5	0·97	0·04	702/802
16	Cannock	Littleton No. 2	Benches	11·6	3·6	0·56	0·06	802
17	Cannock	Littleton No. 2	Heathen	8·0	3·0	0·47	0·06	702

REFERENCES

[1] TER MEULEN, H. *Rec. Trav. chim. Pays-Bas* 48 (1929) 938
[2] YEARSLEY, C. W. *M.Sc. Thesis.* University of London, 1932
[3] BRAME, J. S. S. and KING, J. G. *Fuel, Solid Liquid and Gaseous* 4th ed., p 348. Arnold: London, 1935
[4] CROSSLEY, H. E. *J. Inst. Fuel* 25 (1952) 224
[5] EDGCOMBE, L. J. *Fuel, Lond.* 35 (1956) 38
[6] PRINGLE, W. J. S. *Fuel, Lond.* 36 (1957) 257
[7] MULLIN, J. B. and RILEY, J. P. *Anal. Chim. Acta* 12 (1955) 162
[8] SAMUELSON, O. *Ion Exchangers in Analytical Chemistry*, p 12. Wiley: New York, 1953
[9] HORTON, L. Private communication
[10] Boiler Availability Committee, *Technical Paper No. 3*

The Chlorination of a Medium Rank Coal at Various Temperatures

F. J. PINCHIN

A study of the chlorination of a medium rank caking coal (Maltby Barnsley Brights) under various conditions, using chlorine gas, has shown that the most stable products are produced at the highest reaction temperatures. Conditions used were: 0° to 10°C in aqueous suspension; 20° to 60°C, 270°C below decomposition temperature, 700°C near end of normal carbonizing temperature range, and up to 1100°C in a gas/solid reaction. In addition, the reaction at 270°C in a stream of air and chlorine was studied. With chlorine alone, the maximum chlorine content of the product was 24 per cent (at 700°C); with air and chlorine at 270°C it was 38 per cent. Substitution and dehydrogenation were shown to occur by measuring the hydrogen chloride formed. Presence of chlorine during carbonization (heating to 700°C or 1100°C) considerably reduced the loss of carbon from the coal by partially inhibiting formation of volatile matter.

THE chlorination of coals has been reviewed by J. F. WEILER[1], G. H. THOMSON[2], E. BEYERS and D. VAN ROOGEN[3] and by M. I. SHENBON *et al.*[4]. The present paper records the results of a brief study on the chlorination of a single coal under a range of conditions; no such study has been reported before.

EXPERIMENTAL

Maltby Barnsley Brights (Coal D6) was chlorinated under the conditions summarized below.

(a) *Expts CCW/1–3. (0° to 10°C)*
In a cooled bolt-headed flask fitted with a glanded paddle stirrer, 50 g of coal (– 72 B.S.S.) was suspended in 250 ml water. Chlorine gas was bubbled through, and the excess chlorine, and the hydrogen chloride formed, were absorbed in excess (ice-cooled) 10 per cent sodium hydroxide and determined by titration. In two successive experiments, sodium hydroxide (2 g; CCW/1) or benzoyl peroxide (1 g; CCW/2) were added as possible catalysts; in a third, water alone was used. The results were not significantly different.

(b) *Expt CGS/2 (20° to 60°C)*
A vertical stainless steel tube (1⅜ in. i.d. by 28 in. long) was used as a reactor with 100 g coal (6–18 B.S.S.). Chlorine gas was passed upwards, and excess chlorine, and the hydrogen chloride formed, were absorbed as before.

(c) *Expts CGS/3 and CGS/4. (270°C)*
A vertical glass tube (heated by a Nichrome winding) of 1·5 in. i.d. and 32 in. long was used with 100 g coal (6–18 B.S.S.). The air used in CGS/4 was passed at 0·5 l./min, and was measured on a capillary flowmeter.

(d) *Expt CGS/5. (700°C)*
A special nickel reactor 1·5 in. i.d. and 24 in. long, then widening to 4·9 in.

i.d. for a further 7 in., heated by Nichrome wire, was used with 100 g coal (6–18 B.S.S.). The reactor was designed as a general purpose one for fluorination, etc.; at 700°C with chlorine there was some corrosion. The charge was supported on a porous nickel sinter.

(e) *Expt CGS/6. (up to 1100°C)*
A vertical silica tube (0·6 in. i.d. and 19 in. long) was heated using 10 g coal (— 72 B.S.S.); quartz wool was used to support the coal.

The products of chlorination were black coal-like substances, which appeared brown on grinding. The distribution of the elements in these products is given in *Table 1*. The products were dried in air at 105°C; up to 3 per cent of hydrogen chloride could be lost at this stage. These products possessed some solubility in chloroform, ethanol or ether.

The stability of the chlorinated coals was assessed approximately by the criteria: (*i*) amount of chlorine removed by hydrolysis on refluxing with 10 per cent sodium hydroxide for 6 to 8 hours, and (*ii*) temperature required to release most of the chlorine as hydrogen chloride on heating to above the chlorination temperature (*Table 2*); no free chlorine was observed during this test. Although these tests have no exact significance, the hydrolysis conditions approximate to those required to remove aliphatic and alicyclic chlorine, while the thermal test gives an idea of the stability of the product as a whole.

RESULTS

The results are summarized in *Table 2*.

(a) *Expts CCW/1–3*
Chlorination in aqueous suspension did not appear to depend on the presence of sodium hydroxide or benzoyl peroxide (which are potential catalysts). The chlorine was only loosely bound; about 57 per cent was removed by hydrolysis with 10 per cent caustic soda and 100 per cent was lost (as hydrogen chloride) on heating to 340°C. Reaction was rapid, and apparently complete in 1 to 2 h.

(b) *Expts CGS/2 and CGS/3*
Chlorination at 20° to 60°C was slow and incomplete. At 270°C (just below the carbonizing temperature[5, 6]), reaction was incomplete after 7·6 h. Much of the chlorine was removed on hydrolysis, and all was lost as hydrogen chloride on heating to 550°C.

(c) *Expt CGS/4*
This experiment, in which chlorine and air were passed over the coal, was carried out for a much longer period than any of the other experiments, since oxidation was known to be a slow reaction. It was hoped, by a combination of chlorination and oxidation, to 'open up' the coal structure and to produce a rather different product. This aim was at least partially achieved; the chlorine content (38·4 per cent d.a.f.) was the highest obtained in these experiments, and only half of this chlorine was removed on hydrolysis or on heating to 550°C.

Table 1. Distribution of elements in solid products g/100 g original coal

Table 1. Distribution of elements in solid products g/100 g original coal

Constituent	*D6 coal*	*CCW/1*	*CCW/3*	*CGS/2*	*CGS/3*	*CGS/4*	*CGS/5*	*CGS/6* (*1*)	*CGS/6* (*2*)	*Total*	*Carbonized coal*
C	76·9	70·7	77·6	76·1	76·7	65·2	70·0	42·2	22·8	65·0	61·9
H	4·8	3·2	3·7	4·7	4·0	1·4	1·9	0·9	0·1	1·0	1·3
N	1·6	1·6	1·7	1·6	1·8	1·6	1·6	0·9	0·4	1·3	1·4
S	1·5	1·2	1·2	0·9	0·7	0·5	0·6	0·6	0·2	0·8	0·4
O+*errors*	6·7	9·9	13·2	11·6	16·2	9·0	3·8	*Nil*	*Nil*	*Nil*	1·1
Cl	0·6	29·5	27·0	7·4	14·8	48·6	25·2	8·6	2·4	11·0	—
Ash	3·9	2·5	2·8	4·2	2·9	2·7	4·8	4·1	0·9	5·0	4·7

NOTE: The moisture content of the coals and products is fortuitous, and although taken into account is not quoted here.

Table 2. Chlorination of Maltby Barnsley Brights

Run No.	*Temp. °C*	*Time h*	*Chlorine feed g/h*	*Coal weight g*	*Reaction conditions*	*Coal size B.S.S. sieve*	*Product weight (dry) g*	*Product analysis (% d.a.f.)*						*Chlorine % of total removed by*	
								C	H	N	S	O+*errors*	Cl	*Hydrolysis*	*Heating*
CCW/1	0–10	1·0	—	50	*Aq. susp.*	−72	62	60·8	2·8	1·4	1·1	8·5	25·4	—	—
CCW/3	0–10	1·9	24	50	*Aq. susp.*	−72	66	62·4	3·0	1·4	1·0	10·6	21·6	ca. 60	100 (340°C)
CGS/2	20–60	3·8	44	100	*Gas/Solid*	6–18	108	74·4	4·6	1·6	0·8	11·4	7·3	37	100 (550°C)
CGS/3	270	7·6	31	100	*Gas/Solid*	6–18	118	67·2	3·5	1·5	0·6	14·2	13·0	—	100 (550°C)
CGS/4	270	21·6	14	100	*Air/Gas/ Solid*	6–18	130	51·6	1·1	1·2	0·4	7·1	38·4	ca. 50	50 (550°C)
CGS/5	700	8·0	20	101	*Gas/Solid*	6–18	108	67·9	1·8	1·5	0·7	3·7	24·4	ca. 60	100 (1000°C)
CGS/6	*to* 1100	0·8	12	9·5	*Gas/Solid*	6–18	10·0	*79·3	1·8	1·8	1·2	*Nil*	16·3	—	—
								†88·3	0·5	1·6	0·9	*Nil*	9·2	—	—
								‡82·2	1·3	1·6	1·0	*Nil*	13·9	—	—
Carbonized coal	700	6·0	—	140	—	6–18	99	93·6	1·9	2·2	0·7	1·6	—	—	—
Original coal	—	—	—	—	—	−72	—	83·5	5·2	1·7	1·6	7·4	0·6	—	—

* Product (1). † Product (2). ‡ Combined product.

NOTE: For CGS/4 the time of chlorination was 21·6 h, but the total time (including warming up periods due to intermittent working) was 36·5 h.

(d) *Expt CGS/5*

In this experiment chlorine was passed while the coal was being heated from 375° to 700°C, and at 700°C; chlorine was passing except during the first quarter of an hour of the experiment. By passing chlorine during the bulk of the carbonizing period[5,6], it was hoped to interfere with the carbonization process and obtain a stable product. Little tar (only 2 g) was produced; this was not investigated.

In addition, analyses are presented for a similar sample of coal which was carbonized (in nitrogen at 1 l./min) for six hours under approximately the same conditions; it shows that the presence of chlorine reduces the carbon loss from the coal, i.e. partially inhibits formation of volatile products (e.g. tar).

In expt CGS/5 the chlorine content was 24 per cent; 60 per cent of this was removed by hydrolysis and all was lost as hydrogen chloride on heating to 1000°C.

(e) *Expt CGS/6*

Here the coal was heated rapidly to 1000°C (0·8 h) in a stream of chlorine. The run was terminated by a block in the reactor. The product was sorted mechanically into two parts: (*1*) coal-like, and (*2*) apparently partially graphitized into rods; the hydrogen in this latter material was only 0·5 per cent. A calculated overall analysis for the combined product is also given in *Table 2*.

DISCUSSION

Table 2 shows that with increasing temperatures of chlorination, the product contains chlorine which is more firmly bound; more carbon and hydrogen

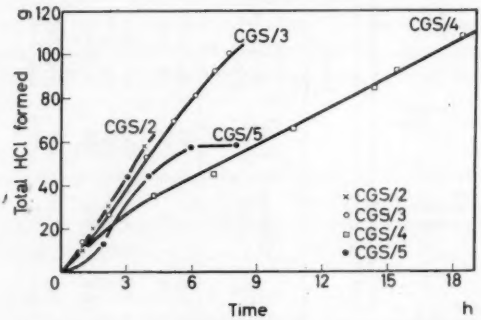


Figure 1. Total hydrochloric acid versus time (basis: 100 g coal)

are lost with increasing reaction temperatures. Much more hydrogen chloride is produced than that equivalent to the chlorine fixed in the product (substitution being assumed to fix half the chlorine molecule and to release the other half as hydrogen chloride); therefore most of the hydrogen is lost in a dehydrogenation reaction, although substitution also occurs. *Figure 1*

shows the amounts of hydrogen chloride released in these experiments; dehydrogenation begins to fall off at 700°C. Such dehydrogenations have been reported previously[1].

No attempts were made to investigate the amounts of tar formed during the chlorinations, but little was observed. The absence of tar formation quoted in the literature[1, 2] is thus qualitatively confirmed. Quantitative confirmation is given in *Tables 1* and *2*, where the carbon and hydrogen losses from the coal are shown to be smaller in these presence of chlorine at 700° to 1100°C than when the coal is heated only in nitrogen at 700°C (carbonized coal).

Traces of white crystals (yield less than 50 mg/100 g coal) were found in the cooler parts of the reactor after the runs at 270°C (CGS/3 and 4); melting points had suggested that the material was hexachlorobenzene, and this was confirmed by comparison of the x-ray diffractograms with those of an authentic sample.

It was not possible to confirm by infra-red spectra that chlorination had occurred, owing to the complicating effects of oxidation; this was usually associated with a reduction in the number of methylene groups.

CONCLUSIONS

With increasing temperatures of chlorination, the chlorine remaining in the product becomes more firmly bound, though much is still removed on hydrolysis. With increasing temperatures there is also more dehydrogenation until 700°C is passed.

Chlorination in the presence of air at 270°C gives a product which has been modified by oxidation; only half the chlorine is removed by hydrolysis, or heating to 550°C, the remainder probably being attached to aromatic rings.

It is concluded that chlorination removes hydrogen and peripheral organic groups, and that this reaction predominates over incorporation of chlorine into the coal nucleus. In addition, if chlorine is present during the carbonization period (heating to 700°C or 1100°C) it considerably reduces the loss of carbon from the coal, i.e. it inhibits tar formation (as previously noted in the literature[7]).

Thus it appears that chlorination, even under relatively severe conditions (700° to 1100°C), does not substantially alter the major part of the coal structure; subsequent carbonization of coals treated at lower temperatures would not produce chlorinated tars, but only hydrogen chloride and some volatile matter. Compared with the fluorination of coal[8], chlorination appears to be unprofitable and ineffective as a means of obtaining useful chemicals. Chlorination, however, can be used for de-ashing coals and cokes at 1400°C[9].

This work was carried out in the Chemistry Department of the British Coal Utilisation Research Association. The author is indebted to Mr D. Flint and the staff of the B.C.U.R.A. Analytical Department for the analyses, to Dr J. K. Brown for the infra-red spectra, to Mr J. D. Watt for the x-ray *examinations,*

to Mr R. L. Bond for some helpful discussions and to the British Coal Utilisation Research Association for permission to publish this work.

British Coal Utilisation Research Association,
Leatherhead, Surrey

(*Received January 1958*)

REFERENCES

[1] WEILER, J. F. *Chemistry of Coal Utilization* (Ed. H. H. LOWRY), Vol. 1, Chap. 8. Wiley: New York, 1945

[2] THOMSON, G. H. *Progress in Coal Science* (Ed. D. H. BANGHAM), p 276. Butterworths Scientific Publications: London, 1950

[3] BEYERS, E. and VAN ROOGEN, D. *J. S. Afr. chem. Inst.* 4 (1951) 97

[4] SHENBON, M. I. *et al. Trud. kharkhovsk. khim.-tech. Inst. Kirova* (*Ukr. khim. Zh.*) 21 (1955) 636; *Chem. Abstr.* 50 (1956) 6771

[5] DRYDEN, I. G. C. *J. Inst. Fuel* 30 (1957) 193

[6] BOLTON, K., CULLINGWORTH, J. E., GHOSH, B. P. and COBB, J. W. *J. chem. Soc.* (1942) 252

[7] ECCLES, A., KENYON, G. H. and MCCULLOCH, A. *Fuel, Lond.* 10 (1931) 4

[8] FARENDEN, P. J. Private communication. *B.C.U.R.A. Members' Inform. Circ. No. 186* (1957). *B.C.U.R.A. Annu. Rep.* (1955) 40; (1956) 36

[9] Aluminium Laboratories Ltd. *B.P. 716 718* (1954)

Thermal Decomposition of Coal in High Vacuum

BOZEN SUN*, C. H. RUOF† and H. C. HOWARD‡

An all-steel molecular distillation apparatus has been constructed for the study of the primary thermal decomposition products of coal. Decomposition in this apparatus of four coals differing widely in rank has shown that the distillate from the coal with strongest agglutinating properties is richest in high molecular weight components. With the Pittsburgh bed coal nearly 50 per cent of the material distilled at 550°C is so high in molecular weight that it remains on a water cooled condenser at a pressure of about 1 micron. The lignite sample gave a higher yield of condensate than the low-volatile, bituminous coal but the fraction of high molecular weight components in the total volatile matter from the former was very small.

All the coals studied, including the Pittsburgh bed, failed to pass through a fluid stage and to form a coherent coke mass under the conditions of this decomposition. There appears little doubt that coke formation is dependent on the liberation of certain high molecular weight but fusible components in the early stages of the decomposition. The molecular still is an ideal tool for studying these initial thermal decomposition products of coal.

ONE of the most valuable analytical tools available to the coal technologist is the proximate analysis. In this very simple test the loss in weight which a sample of coal undergoes, when subjected to pyrolysis under certain arbitrarily chosen but rigidly controlled conditions, is determined. This loss in weight, corrected for the moisture in the original sample, is designated the volatile matter and the weight of the residue corrected for ash, the fixed carbon. Both of these quantities are used extensively in the scientific classification of coals and in their utilization.

Since the 'volatile matter' is not recovered in the proximate analysis no direct information is obtained in this test on the nature of the volatile components evolved. Various types of carbonization assays, which permit satisfactory quantitative recovery of gaseous, liquid and solid pyrolytic products, however, have been developed and from the results of this type of test, information has been obtained on the nature of the volatile matter when coals of different types and ranks are pyrolysed.

In general, high rank coals give lower yields of liquid and solid products and the gases are very rich in hydrogen; those of intermediate rank give high yields of tarry liquids and the gases are rich in methane, while those of low rank may yield tars in varying amounts but the gaseous products are characterized by a high content of carbon dioxide and water.

Indirect information as to the general nature of the volatile products can be obtained from a proximate analysis and calorific determination by calculation of the 'specific volatile index'. This index[1] is the number of calorific

* Present address: Central Research Dept, Monsanto Chemical Co., Dayton 7, Ohio.
† Present address: Mellon Institute, Pittsburgh 13, Pa.
‡ Present address: U.S. Bureau of Mines, Pittsburgh 13, Pa.

units in 1 per cent of volatile matter and hence reflects the richness of the volatile components in hydrogen. It is a maximum with anthracites and a minimum with lignites.

Unfortunately neither the assay methods nor the indirectly calculated indices give satisfactory information of the nature of primary thermal decomposition products of coal. Information concerning these is of particular interest in the coking coal range because it seems very probable that fluidity, agglutinating, swelling and expansion properties as well as the physical properties of the coke are determined to a large degree by the properties of the primary decomposition products. At various times coal investigators have attempted to relate the coking property of coals to a 'coking principle' or 'coking component' which could be isolated from coal by solvent extraction. The view that there is a certain chemical component responsible for coking is certainly not correct, but there appears little doubt that coking depends on the nature and amounts of certain primary thermal decomposition products.

Pyrolysis of coals in high vacuum where secondary reactions are at a minimum results in residual and volatile products of very different properties from those obtained by decompositions at normal pressures. Earlier work has shown[2] that even with a highly fluid coal of strong agglutinating properties, such as that from the Pittsburgh bed, there was no fusion of the particles to a coherent coke mass at temperatures of 550°C and that the volatile products consisted largely of high molecular weight solid bitumens. Low molecular weight liquid hydrocarbons, tar acids and tar bases characteristic of the pyrolytic products from coal at the same temperature under normal pressures were present only in small amounts.

These facts indicate that if the primary decomposition products of a coking coal are withdrawn sufficiently rapidly from the decomposing coal surface, fusion cannot take place and no coherent coke mass will form. It thus appears probable that recovery and examination of these primary decomposition products will extend greatly our knowledge of the mechanism of coke formation and of the origin of the low molecular weight hydrocarbons, tar acids and tar bases characteristic of coal carbonization at normal pressures.

EXPERIMENTAL

Apparatus

For this investigation an all-steel design of molecular still was constructed (see *Figure 1*).

The cylindrical steel vacuum chamber rested directly on the mouth of the diffusion pump and was so constructed that it could be easily assembled and dismantled into its three main component sections: the circular bottom plate, the cylindrical chamber wall, and the circular top plate. The sections were fitted together and held in place by their weight. The surfaces between the sections were carefully machined and for each run were freshly lubricated with Silicone High Vacuum Stopcock Grease (Dow-Corning Corpn), which retained a satisfactory viscosity even at the temperatures encountered in this work. This simple gasketless seal proved entirely satisfactory.

The bottom plate carried the connections to the vapour pump, to the thermocouple wires and to the heater leads. A 60/50 standard taper steel outer member joint (J–101,

Scientific Glass Apparatus Co.) was welded into a 2¼ in. hole in the centre of the bottom plate and projected downward for insertion on the mouth of the diffusion pump.

Four Kovar–glass terminals (Type GC 95.2008, Stupakoff Ceramic & Manufacturing Co., Latrobe, Pa) were soldered into four holes in the bottom plate. The terminals afforded electrical insulation and vacuum-tight seals for the insertion of wires through the steel plate. Into one pair of terminals were soldered the iron and the constantan wires of the thermocouple; and into the other, two 2 in. lengths of copper rods to both ends of which were attached brass binding posts for simplified assembly and dismantling of the heater leads.

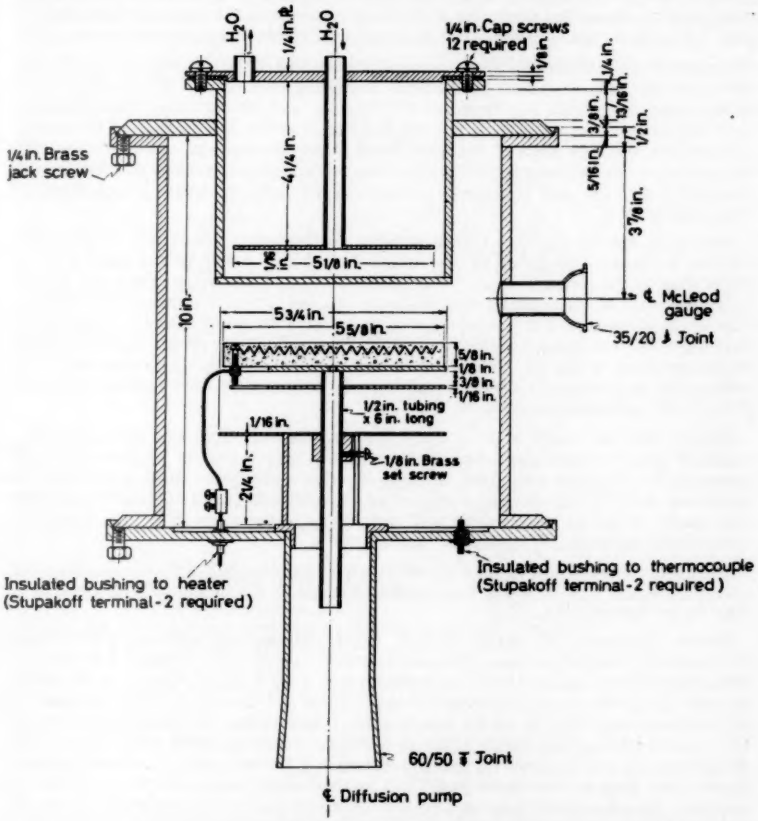


Figure 1. Molecular still

The chamber wall was made of a piece of Shelby seamless steel tubing to the ends of which were welded two steel flanges. The bottom surface of the lower flange was machined and rested on the bottom plate and the top surface of the upper flange was machined to contact the top plate which rested on it. A steel outer member 35/20 spherical joint (SB–101, Scientific Glass Apparatus Co.) was welded into a hole on one side of the chamber wall and served as the connection to a McLeod gauge.

The top plate carried a wide-mouthed condenser. The condenser consisted of a length of Shelby steel tubing welded into the centre of the top plate and projecting downward

vertically into the vacuum chamber. A steel disc was welded horizontally across the bottom of the Shelby tubing to close it off and serve as the condensing surface although small amounts of condensate frequently were found on the Shelby tubing. This condenser design permitted condensation far enough away from the greased seals so that the condensate could be removed by rinsing with solvents without danger of contamination with the grease. The wide mouth permits the use of many alternative refrigerants such as ice, dry ice, or liquid nitrogen. The condenser can be readily converted also to permit use of tap water. The top of the condenser projected above the top plate and carried a machined flange welded to it; a disc bearing a water-inlet tube and a water-outlet can be tightened down on to a gasket fitted to the top of the flange. A baffle plate around the bottom of the water-inlet tube forces the water to spread out over the condensing surface before leaving it.

Alignment of the chamber wall on the bottom plate and of the top plate on the chamber wall is considerably simplified by shoulders extending upward on the periphery of the bottom plate and on the top flange of the chamber wall, respectively. These shoulders serve also as one side of a groove into which Silicone grease can be inserted to ensure a vacuum-tight seal. The edges of the lower flange of the chamber wall and of the top plate were chamfered inward to serve as the other side of these grease grooves. Any leaks which might develop in the seals were easily detected visually since the grease is sucked inward from these grooves.

After each run the chamber was brought to atmospheric pressure and the top plate removed to permit withdrawal of the sample holder and rinsing of the condenser and shield. Due to the cohesive force of the greased surfaces it was found necessary to prise up the top plate off the chamber wall by means of a jack screw. This was a $\frac{1}{4}$ in. SAE cap screw made of brass so that it would not mar the machined steel surfaces of the plates; it was turned into a threaded hole in the top flange of the chamber wall and thrusted upward on the periphery of the top plate to lift it. An identical jack screw was provided in the bottom plate to separate the chamber wall from the bottom plate when alteration or repair of the heater assembly was desired.

Shield—An 8 in. length of 8 in. o.d. cylindrical stainless steel stovepipe served as a radiation shield concentrically located between the heater and the chamber wall and prevented the chamber wall from reaching a temperature above 90°C even when the heater was at 550°C. In addition, it condensed the small amount of material which otherwise would collect on the chamber wall and simplified the recovery of this condensate since it could be lifted out readily for rinsing.

The shield simply slipped in place and rested on the bottom plate of the vacuum chamber; lateral movement was prevented by a shoulder formed by machining an 8 in. circle $\frac{3}{32}$ in. deep on the bottom plate.

Pumps—An electrically heated Type D Gaede 4-stage steel mercury vapour pump (E. Leybold's Nachfolger A.G., Cologne, Germany; supplied by James G. Biddle Co., Philadelphia) was employed to obtain pressures of 1×10^{-5} mm of mercury in the system. In order to keep the distance between the vapour pump and vacuum chamber to a minimum the chamber rested directly on the mouth of the Gaede pump. A Cenco–Hyvac was used as a mechanical backing pump, although a Cenco–Pressovac pump, which has a lower pumping speed, was available for use in capturing and delivering the gases produced in the experiments. Between the vapour pump and the mechanical pump there was a dry ice trap to collect the condensable gases and protect the mechanical pump, a stopcock to vent the apparatus to the atmosphere, and a simple mercury manometer to assist in detection of leaks and possible pump failures.

McLeod gauge—When assembly of the apparatus was first completed a conventional McLeod gauge was used in order to check for leaks and performance of the Gaede pump; an ultimate vacuum of 1×10^{-5} mm of mercury was quickly obtained. This gauge was later replaced by a more rapid acting McLeod gauge of the swinging type (J–4145, Scientific Glass Apparatus Co.). It was attached through an adapter to the spherical steel socket provided on the wall of the vacuum chamber. In order to determine as closely as possible the true pressure at the evaporating surface this gauge was located as near as possible to the evaporating surface. Since it was calibrated only from 0·001 to 1 mm, pressures lower than 0·001 mm of mercury are reported only as 0·001 mm.

Heater assembly—The heater assembly consisted of a heater set upon an adjustable-height pedestal with integral reflecting plates. The heater itself was a 600 W kitchen-type commercial hot plate consisting of a ceramic disc with a spiral groove into which a coiled Nichrome heating element was inserted. It was connected by a pair of copper wires to the inside binding posts on the Stupakoff terminals; the external binding posts were in turn connected through an ammeter to a Type 116 Powerstat (Superior Electric Co.) for regulation of power input. In order to reach temperatures of 550°C for the thermal decomposition of coal it was necessary to use almost the full line voltage of 110 V with a current input of *ca.* 5·1 A. However, small amounts of the wire distilled off at these high wire temperatures and low pressures, and deposited on the ceramic plate rendering it electrically conductive with resulting frequent short circuits and burnouts. This difficulty was overcome by filling the groove level full with Orelectric Cement No. 13 (Orefraction Inc., Pittsburgh 8, Pa) thus embedding the wires.

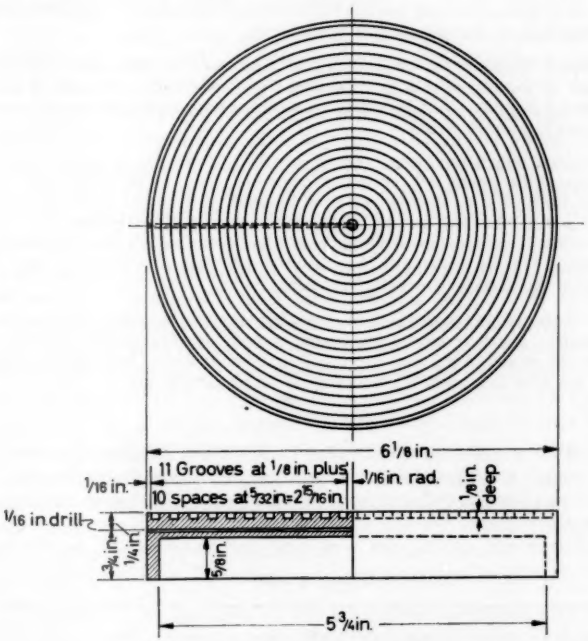


Figure 2. Coal sample pan

The pedestal was designed to allow a maximum of free pumping area for exhaustion of gases and was entirely constructed of stainless steel to decrease heat losses by conduction; its system of horizontal reflecting stainless steel plates minimized heat losses by downward radiation and prevented excessive warming of the bottom plate of the vacuum chamber. The horizontal circular top plate of the pedestal supported the ceramic disc of the heater and, since stainless steel is a poor heat conductor, it prevented excessive losses of heat downward. Another horizontal circular plate 1 cm lower and parallel to this one provided additional reflectance. Both plates were welded to a pedestal rod which passed vertically through a stationary locking-screw type collar; this collar was an integral part of another horizontal circular reflecting plate. This third plate was supported by three legs from a flange-type collar inserted in the upper end of the standard taper joint which rested on the mouth of the Gaede pump. This arrangement provided a 5 cm vertical adjustment of

heater height for experiments on variation of the distance between evaporating and condensing surfaces and ensured coaxial alignment of the heater assembly with the vacuum chamber.

Sample pan—A coal sample pan for molecular distillation of coals posed the most difficult problem encountered in the design of the apparatus. The primary goal of these experiments was to remove and condense the primary pyrolysed fragments as rapidly as they were produced so that they could not undergo further reaction before examination or remain to act as 'solvents'. Thus the coal did not become plastic, and the coal particles remained as separate entities. These particles could only receive their heat by contact with, or radiation from, the sample holder, since at the low operating pressures few gas molecules remain in the voids to transmit heat and since coal is a poor conductor of heat, thus minimizing the heat flowing through one particle to another.

The sample pan (*Figure 2*) was made from aluminium to ensure good heat conduction and distribution and to give a pan light enough to be weighed accurately. It was machined from a 1 in. circular plate of aluminium $6\frac{1}{8}$ in. in diameter.

A series of concentric square-bottomed grooves $\frac{1}{8}$ in. deep and $\frac{1}{8}$ in. wide were machined into the top surface of the pan. These grooves were filled only about half full of coal particles so that the top particles could be heated by radiant energy received from the walls of the grooves protruding above them.

To permit concentric alignment of the sample pan in the vacuum chamber and to prevent possible lateral movement off the heater assembly, the bottom of the pan was machined out to a depth of $\frac{1}{8}$ in. leaving only a $\frac{1}{16}$ in. wide skirt on the periphery. This skirt fitted down over the $\frac{1}{8}$ in. thick ceramic plate of the heater itself completely enclosing its walls and top surface. Heat escaping from the heater had therefore first to pass through the sample pan except for the downward heat losses which were minimized by the top stainless steel plate of the pedestal supporting the heater.

The aluminium in the sample pan was $\frac{1}{4}$ in. thick between the bottom of the grooves and the bottom surface which rested on the heater. A hole was drilled laterally with a No. 52 drill across the radius of the pan into this $\frac{1}{4}$ in. of aluminium. The thermocouple was inserted into this hole to register the temperature of the sample pan.

Coals used

The coals studied were representative of four ranks, a low-volatile bituminous from West Virginia, a high-volatile 'A' bituminous from Pennsylvania, a high-volatile 'C' bituminous from Illinois and a lignite from Texas. Analyses are shown in *Table 1.*

Table 1. Analyses of coals

State	Bed	Condition	Proximate, %				Ultimate, %				
			Moisture	VM	Fixed carbon	Ash	C	H	N	S	O
West Va	Pocahontas	1	0·8	15·3	78·3	5·6					
		2					90·9	4·9	1·5	0·6	2·1
Pa	Pittsburgh	1	1·9	33·6	57·0	7·5					
		2					85·5	5·5	1·7	1·1	6·2
Ill.	Illinois No. 6	1	6·7	33·9	50·3	9·1					
		2					82·6	5·4	2·2	0·9	8·9
Texas	Sandow	1	33·6	28·5	26·5	11·4					
		2					44·5	7·4	0·9	1·3	45·9

Condition 1: sample as received. Condition 2: moisture- and ash-free.

Procedure

The coal samples were ground and screened to give − 40 to + 60 mesh samples which were used without drying. To allow adequate space for swelling of the coal particles during the process only 9 or 10 g of coal was charged to the sample pan; this amount filled the grooves only about half full. The coal particles were compacted by gently tapping on the sides of the pan. The weight of the coal to ± 0·01 g was determined from the weights of the pan full and empty. The loaded pan was then placed on top of the heater pedestal which had been set at the desired height, the thermocouple inserted and the vacuum chamber closed and sealed. The condenser was charged with crushed ice intermittently throughout the run; the water from the melting ice was siphoned off as necessary.

The evacuation with the mechanical pump was carried out slowly to prevent rapid expansion of the air in the voids between the coal particles with a resulting 'blow out' of coal from the sample pan. The rate of evacuation was easily controlled by regulation of a pinch clamp on the hose between the vapour pump and the mechanical pump. The Gaede pump was started when the pressure registered by the manometer was less than 20 mm of mercury, the maximum pressure at which it will operate. Approximately 45 minutes was required to pump the vacuum chamber from atmospheric pressure to the operating vacuum.

As soon as the pressure in the vacuum chamber was less than 0·001 mm of mercury, heating of the sample pan was begun with an input of 4·5 to 5·2 A. Temperatures and pressures were recorded every 5 or 10 minutes; data for a typical run are shown in *Figure 3*. Approximately 90 minutes was required to reach the desired operating temperature which was maintained by manual control of the Powerstat. Rate of evolution of volatile products decreases during the decomposition and it was observed that heat input must be correspondingly lowered to maintain a constant temperature. The volume of gases being liberated at any time was indicated by the pressure readings, since the pumping rate remained constant throughout the experiment. The maximum gas evolution occurred with the Pittsburgh bed coal at 470° to 480°C (cf. *Figure 3*) as indicated by a rise in pressure to several tenths of a millimetre, followed by a decline to less than one micron.

To terminate an experiment, the heater was turned off and the temperature of the pan and contents allowed to fall to 100°C with continued evacuation. When this temperature was reached the vapour pump was turned off and after it had cooled to room temperature the system was opened to atmosphere through the stopcock. As a result of this procedure, neither residue nor condensate were in contact with air at temperatures above ambient.

After the still was opened, the pan containing the non-volatile residue from the coal was weighed and the loss in weight determined. The condensate was a yellow, resinous solid rapidly turning brown on exposure to the air. It was removed from the condenser by washing with 1 : 1 mixture of benzene and alcohol and its weight determined by evaporation of the solvent in a tared beaker. The proportion of 'pentane-insoluble' material was determined by dissolving the dried condensate in 50 ml of benzene and pouring this

benzene solution into 500 ml of pentane. After standing overnight the precipitated 'pentane-insoluble' fraction was filtered off on a tared, fritted glass crucible and dried at 105°C for about 1 hour and weighed.

Sufficient material was not available from the condensates from all of the coals for analysis. A number of the products from the various runs on the

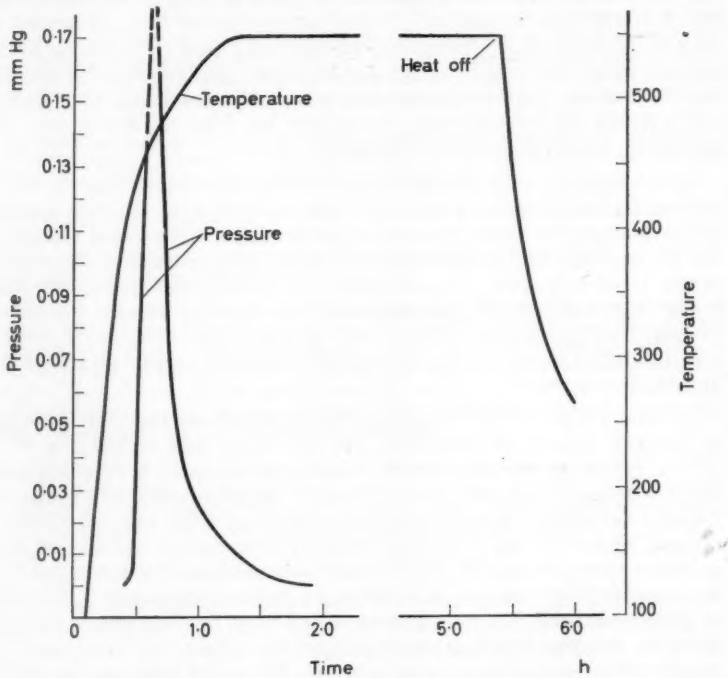


Figure 3. Temperature and pressure versus time during a typical pyrolysis

Pittsburgh bed coal were, however, combined and the following analytical data obtained:

Composition from Pittsburgh bed coal, per cent:
Residue
C, 80·01; H, 3·00; Ash 9·23; O, N, S (by diff.), 7·76; H/C = 0·449

Condensate
Pentane soluble: C, 84·52; H, 7·59; Ash, 0·79; O, N, S (by diff.), 7·10; H/C = 1·07; mol. wt 350
Pentane insoluble*: C, 84·06; H, 5·99; Ash, 0·1; O, N, S (by diff.), 9·85; H/C = 0·85; mol. wt 400

RESULTS AND DISCUSSION

In developing the apparatus and studying its performance some 15 runs

* This analysis refers to that part of the pentane–insoluble material which was soluble in benzene, about 43 per cent.

were made on the Pittsburgh bed coal at temperatures ranging from 500° to 550°C, and for heating periods of 1 to 4 hours. The effects of variations in the distance between evaporating and condensing surfaces and of temperature of the cooling medium in the condenser were investigated over short ranges.

Maximum yields of condensate and minimum yields of residue were observed when the distance from evaporating surface to condenser was 5 cm and when ice–water was used as condenser coolant. Using these conditions and a heating period of 4 hours at 550°C in three runs on Pittsburgh bed coal the yield of 'residue' ranged between 71·5 and 72·4 per cent and of 'condensate' between 15·83 to 16·99 per cent. These results are in satisfactory agreement with the earlier work on this coal[2].

Table 2. Pyrolysis of coals in high vacuum

Coal	*Charge g*	*Residue g*	*Residue % coal*	*Loss in wt %, diff.*	*Condensate g*
Pocahontas	10·73	9·84	91·7	8·3	0·270
	13·01	11·99	92·2	7·8	0·451
Pittsburgh	11·09	8·31	74·9	25·1	1·342
	14·20	10·91	76·8	23·2	1·704
Illinois No. 6	13·04	9·19	70·5	29·5	1·419
	13·22	9·53	72·1	27·9	1·423
Sandow	12·29	6·59	53·6	46·4	0·551
	13·05	7·05	54·0	46·0	0·677

Coal	*Condensate % coal*	*Pentane soluble, g*	*Pentane soluble % coal*	*Pentane insoluble, g*	*Pentane insoluble % coal*
Pocahontas	2·52	0·220	2·0	0·046	0·43
	3·47	0·271	2·1	0·154	1·2
Pittsburgh	12·1	0·725	6·5	0·527	4·7
	12·0	0·929	6·5	0·742	5·2
Illinois No. 6	10·9	0·744	5·7	0·583	4·4
	10·7	0·758	5·7	0·602	4·5
Sandow	4·5	0·416	3·4	0·108	0·88
	5·2	0·528	4·0	0·151	1·16

Data from later experiments comparing the behaviour of the Pittsburgh bed and three other coals are shown in *Table 2*. In these experiments somewhat larger charges of coal were used and tap-water at about 30°C was supplied to the condenser. It will be observed that for the Pittsburgh bed coal the yield of residue is somewhat higher and the yield of condensate lower than obtained under the previous conditions. However, it is believed that the experiments reported in *Table 2* are of comparative value in studying

the thermal decomposition of these coals. The most striking fact brought out is the very much greater content of higher molecular weight components in the primary products from the Pittsburgh bed coal. The average of the two experiments shows almost 50 per cent of the volatile products from this coal to be condensable at about 30°C and 10^{-3} mm of mercury. The corresponding value for both the Pocahontas No. 3 and the Illinois No. 6 coals is 37 per cent while for the lignite it is only 10·5 per cent. The Pittsburgh bed, the Pocahontas and Illinois coals are regarded as coking coals, the lignite is of course not. It thus appears that for a coal to form a coherent coke the first requisite is a high proportion of high molecular weight components in the primary thermal decomposition products. This view is supported by the conclusions of other workers[4]. Fluidity and agglutinating properties appear, however, to be more closely related to the yield of high molecular weight components per unit of coal.

The pentane-insoluble material was incompletely soluble in benzene so that the analytical data refer only to the benzene-soluble fraction. This part of the pentane-insoluble material is significantly higher in molecular weight and in carbon/hydrogen ratio than the pentane-soluble components. It seems probable that it is these components of the distillate which are of special importance in the coking process.

As was previously pointed out even a Pittsburgh bed coal, which becomes highly fluid when heated under normal conditions, did not melt and form a coherent mass under the conditions of these experiments. The individual particles persisted and under the microscope were seen to be only slightly swollen with partly rounded edges. Thus, while in a coke prepared under normal conditions, the coke structure bears no relation to that of the original coal, the residue from molecular distillation appears to represent the original skeletal framework of the 'organized' part of the coal from which the 'unorganized' part has been distilled[3]. In support of this view is the observation that the increase in porosity of the distillation residue over that of the original coal, as determined by mercury and helium density measurements, corresponds approximately to the volume occupied in the original coal by the distilled products.

Coal Research Laboratory,
Carnegie Institute of Technology,
Pittsburgh, Pa

(*Received January 1958*)

REFERENCES

[1] BURROUGH, E. J., SWARTZMAN, E. and STRONG, R. A. *Invest. Fuel Can.* 725 (1933) 36
[2] JUETTNER, B. and HOWARD, H. C. *Industr. Engng Chem.* (*Industr.*) 26 (1934) 1115
[3] HIRSCH, P. B. *Proc. Roy. Soc. A* 226 (1954) 143
[4] SMITH, F. W. and BROWN, R. L. *Proc. Amer. Gas Ass.* 34 (1952) 719

Measurements of Internal Damping and Considerations of the Rheological Behaviour of Coal

N. B. TERRY

The composite oscillator method, using magnetostrictive excitation, has been developed for the measurement of the internal damping of coal samples. The coal specimen, in the form of a rod, is cemented to a Permendur transducer, and the composite rod is excited magnetostrictively to mechanical resonance. From the mechanical resonance curve, a measure of the internal damping of the specimen can be obtained. The measurements, which covered a frequency range from 5 to 90 kc/s, indicate that Barnsley Hards coal exhibits a frequency spectrum of retardation times, the retardation times increasing rapidly as the frequency decreases. Thus this coal behaves in a manner similar to that of a rheological model consisting of a chain of Voigt elements in series with a spring and dashpot. This view is supported by considerations of the creep curve. However, the limitations of the model are illustrated by the fact that some variation of internal damping with amplitude of excitation has also been observed.

IF a thin strip of coal is subjected to a steady bending load, or a cube is subjected to a steady compressive load, the specimen is found to exhibit an instantaneous recoverable elastic deformation, a retarded, but recoverable elastic deformation, and an irrecoverable deformation due to viscous flow[1, 2]. Moreover, measurements that have been made of the elastic constants of coal

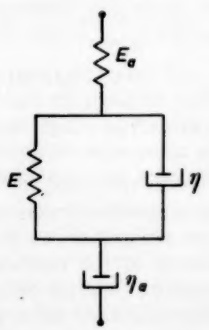


Figure 1. Burgers model of a viscoelastic material

samples have shown that the dynamic Young's modulus, obtained by vibrating a small cylinder longitudinally at kilocycle frequencies, is some 20 per cent higher than the static modulus, measured by compressing a cube of coal or by bending a thin strip[1]. Such behaviour is characteristic of a viscoelastic material, that is to say, a material which responds to an applied stress in a partially elastic and partially viscous manner.

In view of the complex rheological behaviour of such materials, many workers have tried to simplify description by the use of representative models, generally combinations of elastic springs and viscous dashpots. For example, the well known Burgers model, shown in *Figure 1*, is found to give a good representation of the behaviour of many viscoelastic materials. By measuring the dissipation of energy when samples of the material are set into vibration (that is to say, by measuring the internal damping), the reliability of a model can be ascertained, or the model modified if at variance with the experimental results.

There is very little information in the literature about the internal damping in coal. K. INOUYE[3] has made measurements on some Japanese and American coals by vibrating a cantilever of coal at frequencies between 400 c/s and 1·4 kc/s. F. J. HIORNS[4] is engaged on measurements on thin strips of coal set into lateral vibration, by electrostatic excitation, at frequencies below 1·0 kc/s.

The present paper describes some measurements of the internal damping for British coals made at frequencies in the range 5 to 90 kc/s.

EXPERIMENTAL METHOD

If a cylindrical specimen is set into longitudinal vibration in some way, the breadth of the mechanical resonance curve, i.e. a plot of the velocity amplitude of one end of the rod against frequency for a range of frequencies below and above a natural resonance frequency, gives a measure of the internal damping. It is usual to define a mechanical quality factor Q such that

$$Q = f_r/(f_a - f_b) \qquad \ldots\ldots [1]$$

where f_r is a resonance frequency, and f_a and f_b are frequencies equally spaced about the resonance frequency and which correspond to velocity amplitudes $\dot{\xi}_r/2^{\frac{1}{2}}$, where $\dot{\xi}_r$ is the particle velocity amplitude at resonance.

For the present experiments, the coal specimens were cemented (with a thin film of Santolite resin) to polarized Permendur or nickel rods which could be excited magnetostrictively into longitudinal mechanical vibration. As the composite oscillator method, using magnetostrictive excitation, has already been described in detail[5, 6], only a brief description will be given.

The experimental arrangement used is shown in *Figure 2*. The composite rod was suspended at a shallow groove, cut circumferentially midway along the length of the transducer. The earthed suspension consisted of three gramophone needles arranged symmetrically around the circumference. Through coil 1, of value about 10 mH, an alternating exciting current of a few milliamperes was passed after connecting it to the output of a decade oscillator. In this way the composite rod was set into mechanical vibration; the maximum strains were of the order 10^{-5} to 10^{-6}. The output of the detecting coil 2 was measured by the voltmeter V_2 for the range of frequencies about a mechanical resonance. The voltage output of the decade oscillator was adjusted for each frequency to keep the reading of the voltmeter V_1 (placed across a 10 ohm resistor) at a constant level; this ensured that the

exciting magnetic field of coil 1 was kept at constant amplitude. The mechanical resonance curve was measured by plotting the readings of V_2 (the detected voltage is proportional to the mechanical velocity amplitude) against frequency.

After measuring the mechanical resonance curve of the composite rod, the specimen was removed from the transducer by snapping the cement joint, and the resonance curve for the transducer measured.

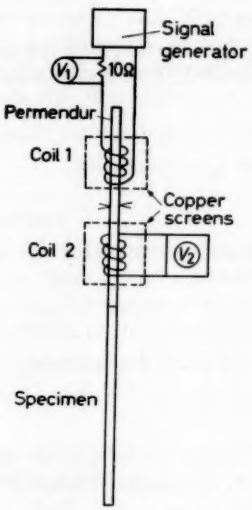


Figure 2. Experimental arrangement for measuring internal damping in coal specimens

The mechanical quality factor for the specimen Q_2 can be shown[7] to be given by

$$Q_2 = Q_T/\{1 + (m_1/m_2)(1 - Q_T/Q_1)\} \quad \ldots . [2]$$

where m is the mass of a cylinder, and subscripts T, 1 and 2 refer to the composite rod, transducer and specimen respectively.

The validity of equation 2 was investigated by experiments with ebonite specimens. Ebonite is useful in that its acoustic properties are very similar to those of coal but, unlike the latter, ebonite is homogeneous. The measurements showed that with the apparatus available, the results were reproducible to within about 2 per cent. For this order of accuracy small differences of cross section between specimen and transducer were not of great importance.

In the derivation of equation 2 it is assumed that each component of the composite rod contains an integral number of half wavelengths. For ebonite it was found that to obtain an accuracy of 2 per cent, the necessary condition is

$$0{\cdot}995 \leqslant n_2 f_2/f_1 \leqslant 1{\cdot}005 \quad \ldots . [3]$$

where f_2 is the natural frequency of the transducer and f_1 that of the specimen.

If, as in these experiments, the specimen, when vibrating as a component of the composite rod at a frequency f_T, is equal or very nearly equal in length to n_2 half wavelengths, $n_2 f_2$ is given by[7]

$$n_2 f_2 = f_T + (m_1/m_2)(f_T - f_1) \quad \ldots\ldots [4]$$

The elastic wave velocity c_2 is given by

$$c_2 = 2l_2 f_2 \quad \ldots\ldots [5]$$

where l_2 is the length of the specimen and, if the specimen is a thin cylinder, the dynamic Young's modulus is given by

$$E_2 = c_2^2 \rho_2 \quad \ldots\ldots [6]$$

where ρ_2 is the density.

THEORETICAL CONSIDERATIONS

A general expression for the elastic wave configuration in a vibrating cylinder is given by

$$\xi_{(x,t)} = e^{j\omega t}(A_1 e^{rx} + A_2 e^{-rx}) \quad \ldots\ldots [7]$$

where ξ is the displacement,

$$r = \alpha + jk \quad \ldots\ldots [8]$$

$k = \omega/c$, $\omega = 2\pi f$, f is the frequency, α is the attenuation constant and A_1 and A_2 are arbitrary constants.

In order to relate the mechanical quality factor Q to the attenuation constant α, it is necessary to formulate and solve the differential equation of motion of the vibrating cylinder. This can only be done, however, by assuming a model describing the viscoelastic behaviour of the solid. The Burgers model, shown in *Figure 1*, is the simplest mechanical model that, on application of a steady stress σ, can exhibit:

(*i*) an instantaneous elastic response (this is due to the action of the elastic spring E_a),

(*ii*) an irrecoverable viscous flow (this is due to the action of the viscous dashpot η_a), and

(*iii*) a retarded but recoverable elastic response (this is due to the action of the Voigt element, i.e. the spring E in parallel with the dashpot η).

W. T. A. MORGANS and N. B. TERRY[1] and C. D. POMEROY[2] have shown that that coal exhibits such behaviour under an applied static load so that, to a first approximation, theoretical considerations of the dynamic behaviour of coal samples should be based upon the Burgers model. As a full description by the author of a vibrating cylinder, of a material assumed to behave as a Burgers solid has already been given[8], the treatment will only be outlined here.

For the Burgers model, the differential equation of motion is

$$\frac{\partial s}{\partial t} = \frac{\sigma}{\eta_a} + \frac{\sigma}{\eta} + \frac{1}{E_a}\frac{\partial \sigma}{\partial t} - \frac{Es}{\eta} + \frac{E}{\eta\eta_a}\int \sigma \, dt + \frac{E\sigma}{\eta E_a} \quad \ldots . [9]$$

where the strain is given by $s = \partial\xi/\partial x$, and σ is the applied stress. Also if

$$1/E_s = 1/E_a + 1/E \quad \ldots . [10]$$

E_s is the modulus of the linear combination of springs E_a and E and corresponds, therefore, to the static modulus. On the other hand, at very high frequencies of applied stress, only the spring E_a will be deformed; E_a is therefore the dynamic modulus measured at very high frequencies.

For a static stress σ applied at time $t = 0$, equation 9 has the solution

$$s_{(t)} = \sigma\left\{\frac{1}{E_a} + \frac{t}{\eta_a} + \frac{[1 - e^{(-t/\tau)}]}{E}\right\} \quad \ldots . [11]$$

The first term on the RHS of equation 11 represents the instantaneous elastic response, the second term the irrecoverable viscous flow, and the third term the recoverable but retarded elastic response. The retardation time is defined as $\tau = \eta/E$. Equating the force on an element of the cylinder to the mass acceleration of the element we obtain

$$\partial\sigma/\partial x = \rho(\partial^2\xi/\partial t^2) \quad \ldots . [12]$$

Differentiating equation 9 with respect to both x and t, and using equations 7, 8 and 12 we have, on equating real and imaginary parts,

$$2\omega\tau ak - (a^2 - k^2) - \rho\omega^2/E_s = 0 \quad \ldots . [13]$$

and

$$\tau\rho\omega^3/E_a + 2ak + \omega\tau(a^2 - k^2) = 0 \quad \ldots . [14]$$

Equations 13 and 14 connect the retardation time with the attenuation constant. By applying the wave function of equation 7 to the differential equation of motion 9, and applying the boundary conditions that (*i*) the stress is zero at the free end of the cylinder, say at $x = 0$, (*ii*) at the other end of the cylinder, say at $x = l$, the stress σ is equal to the applied exciting stress $Fe^{j\omega t}$ for all values of t, we may show that the maximum velocity amplitude at the free end of the cylinder is given by

$$\dot{\xi}_0 \propto 1/\{\sin^2(\omega l/c) + \sinh^2 al\}^{\frac{1}{2}} \quad \ldots . [15]$$

so that resonance occurs when $\sin \omega l/c = 0$, i.e. when $\omega l/c = n\pi$ where n is an integer denoting the number of the harmonic.

From equations 1 and 15, remembering that frequencies f_a and f_b correspond to velocity amplitudes $\dot{\xi}_r/2^{\frac{1}{2}}$, we may show that

$$a = \{\sinh^{-1}(\sin n\pi/2Q)\}/l \quad \ldots . [16]$$

MEASUREMENTS ON COAL SAMPLES

General considerations

The measurements were carried out on specimens cut from the coals listed in *Table 1.*

Table 1. Sources of coal specimens

Colliery	*Seam*	*N.C.B. Coal Rank Code No.*	*Approximate VM %*	*Density (helium) g/cm³*	*Description*
Rossington	*Barnsley Hards*	801	33·9	1·364	*Very strong dull coal*
Pentremawr	*Pumpquart*	100a	7·2	1·499	*Anthracite*
Crosshands	*Big*	100a	7	—	*Anthracite*
Oakdale	*Meadow*	301	21·9	—	*Friable weak coal*

All the specimens were rods of rectangular cross section, and were cut by using thin high-speed grinding wheels so that their axes were parallel to the bedding plane; no attempt was made to orient the specimens in any particular direction with respect to the cleat planes. All specimens were air dried, and there was no temperature or humidity control, measurements being carried out under room conditions in the range 18° to 25°C with humidity averaging 55 per cent R. H. For all measurements the lengths of the specimens were adjusted by grinding until the inequality 3 was satisfied.

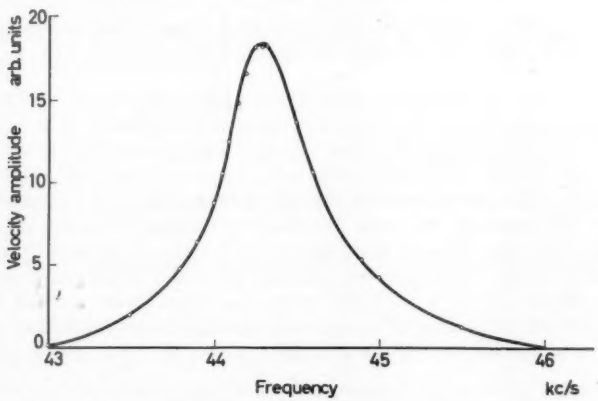


Figure 3. Mechanical resonance curve of a Barnsley Hards specimen cemented to a Permendur rod

Comparison between coals

In order to compare the magnitude of the internal damping of the different coals described above, measurements were made on specimens of lengths ranging from 3 to 12 cm, all of approximately $\frac{1}{16}$ in. square cross section. The transducers used were of $\frac{1}{16}$ in. diameter, and the composite rods were

vibrated in the frequency range from 40 to 60 kc/s. A typical resonance curve for a Barnsley Hards specimen, cemented to a Permendur transducer is shown in *Figure 3*; in some cases the resonance curves were found to be positively skew, although the skewness was too slight to affect the accuracy of the calculations. The results of the measurements are shown in *Table 2*.

Table 2. Internal damping measurements for different coals

Coal	*Transducer*	*Frequency of composite rods kc/s*	*Mechanical quality factor of specimen*	*Attenuation constant* $cm^{-1} \times 10^3$
Barnsley Hards	*Nickel*	41·0	58	13
	Nickel	41·3	56	14
	Nickel	41·3	53	14
	Nickel	41·3	50	15
	Nickel	41·1	61	13
	Permendur	41·4	59	13
	Permendur	41·4	57	13
	Permendur	44·0	55	15
	Permendur	41·5	50	15
	Permendur	41·5	51	15
Crosshands Anthracite	*Permendur*	44·0	130	5·6
	Permendur	43·9	92	7·9
	Permendur	49·6	130	6·5
Pentremawr Anthracite	*Permendur*	61·7	180	5·7
	Permendur	47·9	140	5·7
	Permendur	42·0	160	4·4
	Permendur	61·6	180	5·7
	Permendur	44·1	270	2·7
	Permendur	56·8	110	8·6
Oakdale	*Permendur*	48·2	48	19
	Permendur	48·7	13·5	100
	Permendur	43·9	77	12

Except for the Barnsley Hards specimens, there is a large scatter of results. This is undoubtedly due to the presence of cracks and flaws in the specimens and in fact only the Barnsley Hards specimens could be prepared without obvious flaws. The scatter was particularly large for the very friable Oakdale, and it was concluded that of the coals available only Barnsley Hards was sufficiently homogeneous to be useful for a systematic study of damping. The results do show, however, that the damping in anthracite is considerably lower than for the bituminous Barnsley Hards in spite of the larger number of flaws present in the former. This result might be expected from the brittle nature of anthracite and it is interesting to note that the creep viscosity, η_a, of anthracite is at least an order higher than that for Barnsley Hards[2].

Variation of damping with amplitude of excitation

It was observed that the damping was dependent upon the amplitude of excitation. The results shown in *Table 3* are for measurements made on particular samples of Barnsley Hards at different levels of excitation, the latter being varied by changing the value of the alternating current flowing through through the exciting coil. For these experiments, the Permendur transducers

were of $\frac{3}{16}$ in. diameter and were vibrated as half-waves; the specimens were of approximately $\frac{3}{16}$ in. square cross section and were vibrated as two or three half-waves.

The output of the receiving coil is proportional to the velocity amplitude and therefore, at a given frequency, to the stress amplitude. The results indicate that in general the damping increases with stress amplitude over the

Table 3. The variation of mechanical quality factor with amplitude of excitation for Barnsley Hards coal

Specimen No.	*Resonance frequency of composite rod c/s*	*Length of specimen cm*	*Output of receiving coil mV*	*Mechanical quality factor of specimen* Q_2
1	9057	19·21	0·7	74·9
			3·6	70·5
			12·0	68·5
			38·0	68·9
			75·0	71·6
2	9060	19·21	0·7	80·4
			1·0	77·3
			12·0	76·6
			39·0	74·4
			75·0	77·5
3	5787	44·15	0·37	71·2
			0·75	69·4
			1·2	64·8
			3·7	64·6
4	5780	45·31	0·37	91·3
			0·75	85·9
			1·2	79·6
			3·5	79·5
			6·6	82·5

range examined; this cannot be predicted from the models described in this paper and illustrates their limitations. No variation of the resonance frequency (and therefore the dynamic Young's modulus) could be detected. For a precise study of these effects it would be necessary to measure the absolute amplitude of vibration of the coal specimen; this could be achieved by measuring the change of capacity between the end of the specimen and a condenser plate placed close to it.

Variation of damping with frequency

In order to measure the effect of frequency on the internal damping and dynamic modulus, the composite rods were excited at a number of different resonance frequencies corresponding to the fundamental (or first harmonic) and higher odd harmonics of the transducer, and the mechanical resonance curves were measured for each mode of vibration. The procedure was repeated, after breaking the cement joint, for the Permendur transducer vibrating alone in its odd harmonic modes. For all the frequencies excited therefore the suspension

at the midpoint of the Permendur rod corresponded in position to an amplitude node, so that very little energy was lost through the suspension. The specimens used were those described in *Table 3.*

Since the damping is somewhat dependent on the dynamic stress amplitude, in the ideal experiment the latter would be kept constant at each harmonic frequency. This was not possible with the present arrangement since because of eddy current losses the received voltage is not a reliable method of comparing amplitudes at different frequencies. It had to be assumed that the variations in damping observed for the different harmonics were in fact primarily due to changes of frequency, and that variations due to any changes in the stress amplitude were of secondary importance. Since the variations in Q_2 for the very large amplitude changes described above were much less than the variations observed with changes of frequency, the assumption was considered to be reasonable.

From measurements on the mechanical resonance curves, the attenuation constant corresponding to a particular harmonic frequency could be calculated from equations 1, 2 and 16. The elastic wave velocity was calculated

Table 4. The variation of attenuation and retardation time with frequency for Barnsley Hards

Specimen No.	*Harmonic resonance frequency of composite rod c/s*	*Velocity of elastic waves in specimen cm/s* $\times 10^{-5}$	*Dynamic Young's modulus of specimen dyne/cm²* $\times 10^{-10}$	*Attenuation constant* $cm^{-1} \times 10^3$	*Retardation time sec* $\times 10^5$
1	1 × 9057	1·745	4·15	2·3	30
	3 × 9069	1·75	4·18	7·2	10
	5 × 9062	1·74	4·13	13·6	5·0
	7 × 9049	1·73	4·08	25·1	2·6
	9 × 9043	1·725	4·06	37·3	1·6
2	1 × 9060	1·74	4·13	2·1	31
	3 × 9068	1·74	4·13	8·4	7·9
	5 × 9079	1·75	4·18	14·1	5·1
	7 × 9061	1·73	4·08	23·4	2·8
	9 × 9057	1·73	4·08	40·5	1·6
3	1 × 5787	1·71	3·99	1·5	39
	3 × 5797	1·72	4·04	4·6	13
	5 × 5787	1·71	3·99	9·3	6·0
	7 × 5786	1·71	3·99	11·2	5·2
	9 × 5778	1·70	3·94	15·0	3·7
	11 × 5784	1·71	3·99	17·4	3·3
	13 × 5777	1·70	3·94	18·0	2·9
	15 × 5774	1·70	3·94	14·3	3·8
	17 × 5760	1·69	3·90	18·0	2·8
4	1 × 5780	1·75	4·18	1·1	63
	3 × 5774	1·74	4·13	4·5	15
	5 × 5771	1·74	4·13	9·1	7·3
	7 × 5772	1·74	4·13	13·8	4·9
	9 × 5773	1·74	4·13	17·4	4·0
	11 × 5775	1·745	4·15	14·1	5·0
	13 × 5774	1·745	4·15	18·5	3·8
	15 × 5769	1·74	4·13	13·9	4·8
	17 × 5769	1·745	4·15	15·8	4·3

from equations 4 and 5 and the dynamic Young's modulus was calculated from equation 6. In a previous publication[1], the static Young's modulus, obtained by compressing twenty 1·5 in. cubes of Barnsley Hards in a direction parallel to the bedding plane, has been shown to be $3{\cdot}35 \times 10^{10}$ dyne/cm^2 (standard error $0{\cdot}09 \times 10^{10}$ dyne/cm^2). Using this value, the retardation times for the various frequencies were calculated from equation 13.

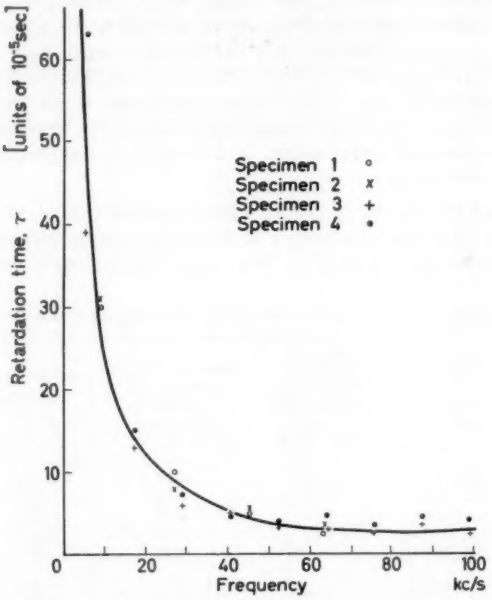


Figure 4. Variation of retardation time with frequency for Barnsley Hards coal

Because of the porous nature of coal, the static modulus of the basic coal material may be somewhat higher than the value given above. However, since it is not possible at the present time to assess the effect of porosity for either the static or dynamic measurements, it is assumed for these calculations that differences between static and dynamic moduli are due entirely to the viscoelastic behaviour of the coal. Values obtained for the dynamic Young's modulus, velocity of sound, attenuation constant, and retardation time for four different specimens of Barnsley Hards at different frequencies are given in *Table 4*; these results are based upon the model shown in *Figure 1*. A plot of the retardation time for each specimen as a function of frequency is given in *Figure 4*.

DISCUSSION OF RESULTS

Frequency variation of retardation time

Figure 4 shows that the retardation time increases rapidly with decreasing frequency of measurement. If the coal could be represented by a model of

the type shown in *Figure 1*, possessing a single Voigt element (the Voigt element consists of the spring and dashpot in parallel), the retardation time τ would be a constant independent of frequency. The results, however, indicate that there is a frequency spectrum of retardation times. A more representative model, therefore, is that shown in *Figure 5* having a series chain of

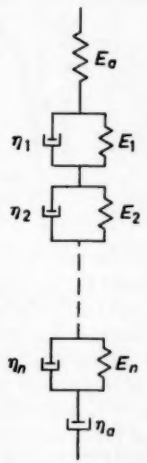


Figure 5. Model of a viscoelastic material exhibiting a number of different retardation times

Voigt elements. The mechanical losses associated with a particular Voigt element will be maximum when the time scale of the experiment is of the same order of magnitude as the retardation time of the element, i.e. when $f \simeq 1/2\pi\tau$. As the frequency is varied, different retardation units contribute to the mechanical losses.

Some substantiation of these considerations can be obtained by a careful consideration of the creep curves. A typical creep curve for a 1·5 in. cube of Barnsley Hards is shown in *Figure 6* and is due to Morgans and Terry[1] (stress $1{\cdot}36 \times 10^8$ dyne/cm^2 applied in a direction perpendicular to the bedding plane). The instantaneous elastic component of strain σ/E_a is not shown in *Figure 6*.

Equation 11 shows that if the model possesses a single Voigt element the retarded elastic strain is given by $S' = \sigma\,(1 - e^{-t/\tau})/E$; for the model of *Figure 5* the retarded elastic strain is given by

$$S' = \sigma \sum_{1}^{n} (1 - e^{-t/\tau_n})/E_n \qquad \ldots\ [17]$$

If we assume that the coal specimens can be represented by the model shown in *Figure 5* the creep curve shown in *Figure 6* can be represented by

$$S = \sigma \left\{ \frac{t}{\eta_a} + \sum_{1}^{n} \frac{(1 - e^{-t/\tau_n})}{E_n} \right\} \qquad \ldots\ [18]$$

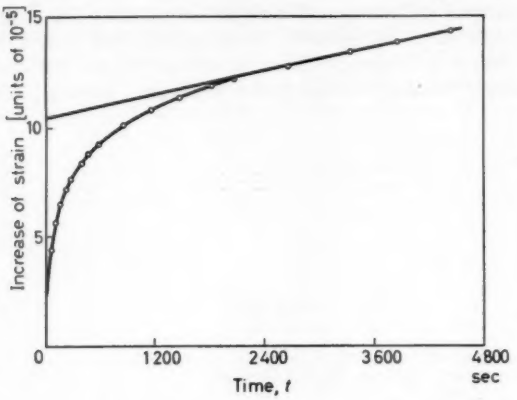


Figure 6. Creep curve for a 1·5 in. Barnsley Hards cube (stress $1{\cdot}36 \times 10^8$ dyne/cm²)

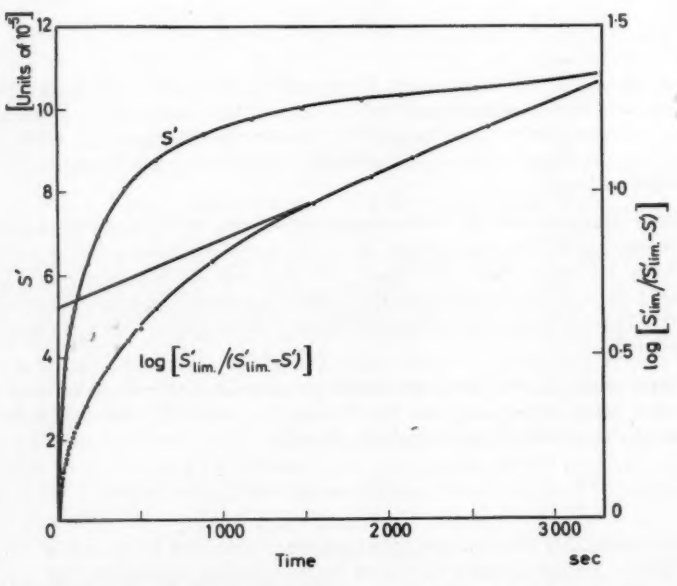


Figure 7. Curves of S' and $\log\left[S'_{\lim.}/(S'_{\lim.}-S')\right]$ for a 1·5 in. Barnsley Hards cube (stress $1{\cdot}36 \times 10^8$ dyne/cm²)

From the slope of the linear portion of the creep curve, a value for η_a of $1{\cdot}6 \times 10^{16}$ poise is obtained. A plot of

$$S' = S - \frac{\sigma t}{\eta_a} = \sigma \sum_1^n \frac{(1 - e^{-t/\tau_n})}{E_n} \quad \ldots . [19]$$

is shown in *Figure 7* and the limiting value is estimated from this graph as 11×10^{-5}, i.e.

$$S'_{\text{lim.}} = \sigma \sum_1^n \frac{1}{E_n} \simeq 11 \times 10^{-5} \quad \ldots . [20]$$

Equation 19 may be written in the form

$$\log \left\{ \frac{S'_{\text{lim.}}}{S'_{\text{lim.}} - S'} \right\} = \log \left\{ \sum_1^n \frac{1}{E_n} \Big/ \left(\sum_1^n \frac{e^{-t/\tau_n}}{E_n} \right) \right\} \quad \ldots . [21]$$

A plot of the LHS of equation 21 as a function of t is shown in *Figure 7*. If a single Voigt element were operating, the RHS of equation 21 shows that the curve would be a straight line of slope $1/\tau$. *Figure 7* shows that this is not in fact so, since at low values of t the slope of the curve decreases rapidly with increasing t. From a careful consideration of the RHS of equation 21, it may be shown that the high initial gradients of the curve are due to terms in the expansion for which τ_n is small; thus the creep curve observed is similar to that which would be obtained from the model shown in *Figure 5*. The slope of the linear portion of the curve of *Figure 7* gives a measure of the largest retardation times operating when a cube of coal is compressed (because of the difficulty of estimating $S'_{\text{lim.}}$ accurately, the position of the final portion of the curve corresponding to equation 21 cannot be determined precisely). The value obtained of 2 500 seconds is seven orders higher than the values ob-obtained from the dynamic measurements; the latter are, however, rising rapidly with decreasing frequency (see *Figure 4*).

Dynamic modulus

It can be seen from the results shown in *Table 4* that there is no marked variation with frequency of the values obtained for the elastic wave velocity and the dynamic Young's modulus, although there is a tendency for the values to decrease slightly with increasing frequency. The velocity of propagation of elastic waves along a viscoelastic rod should be subjected to two opposing effects when the frequency is increased; there should be an increase in velocity due to the viscoelastic behaviour of the material and a decrease in velocity due to the effects of lateral dilatation.

The effect of viscoelastic behaviour can be estimated from equations 6 and 14. From these we have

$$E_{(\omega)} = E_a(1 - a^2c^2/\omega^2 - 2ac/\omega^2\tau) \quad \ldots . [22]$$

From the values obtained for c and τ (see *Tables 2* and *4*) it is clear that even for the lowest frequencies used in these experiments ($a^2c^2/\omega^2 + 2ac/\omega^2\tau$) $\ll 1$, so that no detectable variation of $E_{(\omega)}$ would be obtained over the frequency

range examined. Thus the dynamic modulus measured is very nearly equal to E_a. Nevertheless, as the frequency is reduced, the dynamic modulus must approach the value of the static modulus and evidently these variations must occur at frequencies below those used in this work.

The effects of lateral dilatation have been considered in some detail by D. BANCROFT[9]. As the ratio of the lateral dimensions of the specimen to the wavelength increases, the wave velocity along the rod decreases; from the results given by Bancroft, it may be shown that for the coal specimens used, the elastic wave velocity should decrease by about 2 per cent as the frequency changes from 5 to 90 kc/s. The results in the first three specimens do show a decrease of about this magnitude although, as the effect is small, it is masked to some extent by an irregular scatter of results. The latter is due to variations in the dynamic stress pattern with frequency. Each harmonic frequency is characterized by a particular dynamic stress pattern, while the specimen presents a fixed pattern of microflaws and inclusions. Thus for different harmonics, the antinodal regions of maximum stress occur at different positions with respect to the microflaws, and irregular variations of the measured dynamic moduli as well as the measured damping are observed.

The author wishes to thank Mr I. Evans, and his other colleagues at the Mining Research Establishment for their cooperation during the course of this work. In particular he is grateful to Mr W. T. A. Morgans for helpful discussion. This communication forms part of the research programme of the Mining Research Establishment of the National Coal Board and is published by permission of Dr W. Idris Jones, Director-General of Research. The views expressed are those of the author and not necessarily those of the Board.

Mining Research Establishment,
National Coal Board,
Isleworth, Middlesex

(*Received February 1958*)

REFERENCES

[1] MORGANS, W. T. A. and TERRY, N. B. *Fuel, Lond.* 37 (1958) 201
[2] POMEROY, C. D. *Nature, Lond.* 178 (1956) 279
[3] INOUYE, K. *Bull. chem. Soc. Japan* 26 (1953) 84
[4] HIORNS, F. J. *Fuel, Lond.* 32 (1953) 113
[5] TERRY, N. B. and WOODS, H. J. *Brit. J. appl. Phys.* 6 (1955) 322
[6] TERRY, N. B. *Brit. J. appl. Phys.* 8 (1957) 270
[7] MARX, I. *Rev. sci. Instrum.* 22 (1951) 503
[8] TERRY, N. B. *Proc. phys. Soc. Lond.* 71 (1958) 973
[9] BANCROFT, D. *Phys. Rev.* 59 (1941) 588

Wet Oxidizability of Coal using Phosphoric Acid–Potassium Dichromate Solution

H. HONDA and Y. HIROSE

Wet oxidizability of coals by the solution of potassium dichromate in phosphoric acid has been measured over the range from lignite to meta-anthracite. Wet oxidizability has been evaluated by the fraction of coals decomposed in 150 minutes. The resistivity of coals to wet oxidation is hardly affected by the internal surface area of coals and has an intimate relation with the mechanical properties of coals such as hardness and Young's modulus. Consequently the wet oxidizability of coals depends more upon the persistence or decay of the bridge linkages or cross-linkages and the hydrogen bonds, etc., among the coal base units with the coalification than the increase of condensed aromatic rings of the coal base units. The effect of the large condensed aromatic rings and their stacking in the wet oxidation of phosphoric acid–potassium dichromate solution appears as meta-anthracite having a graphite-like layer.

THE wet oxidizability of carbon for the solution of potassium dichromate in phosphoric acid has been used by H. L. RILEY and others[1] to estimate the crystalline structure of carbon. It was suggested by H. L. RILEY *et al.*[1–5] and H. AKAMATSU *et al.*[6] that the rate of wet oxidation of carbon is proportional to the surface area of the sample and becomes higher as the species is progressively graphitized, that the resistance of carbon to the oxidizing solution is attributed mainly to the presence of the bonding of hydrogen and the cross-linkages between the layer planes of crystallites, and that the swelling destruction of the crystallite micelles by the solution and the dispersion of the crystallite into the solution are an important factor of the reaction. Consequently the measurements of wet oxidizability of coals by the solution of potassium dichromate in phosphoric acid may provide an insight into the structure and properties of coals.

APPARATUS AND PROCEDURE

Carbon is oxidized to carbon dioxide by the solution of potassium dichromate in phosphoric acid. H. L. RILEY *et al.*[1–5] compared the reactivity of various carbons by the weight of carbon dioxide evolved in 150 minutes from a 1 g sample. H. AKAMATSU[6] measured the volume of carbon dioxide produced from a few 10 mg samples. The present authors have used the volumetric method modified to give more reproducible measurements of the initial state of the reaction. In general, the reactivity of carbon is compared by the quantity of carbon dioxide evolved or the quantity of carbon decomposed calculated from the carbon dioxide produced. In order to compare the various coals from lignite of about 60 per cent carbon content to anthracite of about 95 per cent carbon content the quantity of decomposed carbon from the coal has been calculated from the evolution of carbon dioxide.

The apparatus employed in the test is shown in *Figure 1*. The apparatus is made up from the liquid vapour bath, A, with the taper jointed reflux

condenser, B, the glass capillary tube, C, which has the sample holder, D, and the reaction vessel, E, of 30 cm^3 on one end and the ball joint, F, on the other. The gas burette, G, of 50 cm^3 is joined with the glass capillary tube, C, by the ball joint, F. The liquid vapour bath contains water or organic solvent having the required boiling point and is heated by the electric flask heater, H,

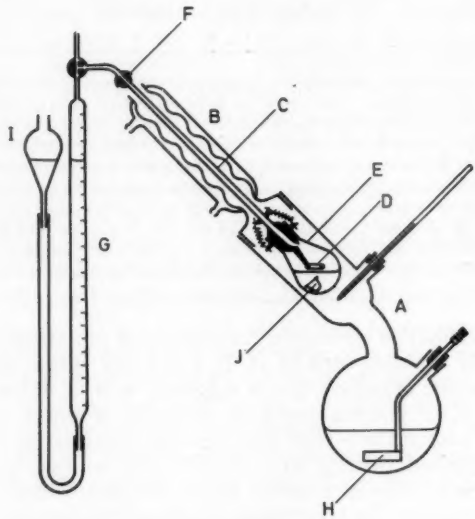


Figure 1. Apparatus

controlled by a suitable variable resistor. The gas burette is connected to the levelling bulb, I, filled with a saturated aqueous solution of sodium chloride.

The oxidizing solution was prepared by adding 10 g of recrystallized extra pure potassium dichromate to 100 g of extra pure concentrated phosphoric acid of which the density at 25°C is 1·70 and by completely dissolving the potassium dichromate under the condition of heating at 120°C for 3 hours. This oxidizing solution was stored in the large burette connecting the calcium chloride tube.

The coal specimen was pulverized to pass through a 30 and stand on a 60 Tyler mesh sieve. The vitrain, of specific gravity less than 1·30, was isolated by the float-or-sink method using mixtures of benzene and carbon tetrachloride. This vitrain was repulverized to pass through a 200 and stand on a 250 Tyler mesh sieve, air dried at 105°C for one hour and stored in the calcium chloride desiccator. The characteristics of the various vitrains are listed in *Table 1.*

About 30 mg of the dried sample was weighed into a small glass weighing cup, J in *Figure 1*, and this cup is settled on the sample holder. The reaction flask containing about 10 ml of the oxidizing solution is attached to the

capillary tube by the hook and spring. The condenser is connected to the capillary tube equipped with the sample and the reaction flask, and joined to the liquid vapour bath. The ball joint of the capillary tube passed through the condenser is connected with the gas burette by a clip. The three-way cock of the gas burette is opened to the air and the liquid vapour bath is heated.

Table 1. Analysis of various vitrains

Vitrains	*Proximate analysis* %				*Ultimate analysis (d.a.f.)* %		
	Moisture	*Ash*	*VM*	*Fixed carbon*	C	H	O+N+S
Kanagasaki	—	7·29*	—	—	64·14	5·20	30·66
Ōhira	12·86	5·84	45·33	35·97	65·10	4·93	29·97
Tempoku—First seam	—	2·07*	—	—	68·12	5·63	26·25
Kaminoyama	—	5·39*	—	—	70·59	5·83	23·58
Nakagō—Under seam	11·19	4·75	38·41	45·65	70·92	4·65	24·43
Taiheiyō	5·68	6·35	—	—	74·10	6·38	19·52
Nakagō	13·32	3·96	38·03	44·69	74·33	5·26	20·41
Tsuzura	—	5·14*	—	—	75·46	6·29	18·25
Kashima	4·11	5·02	50·73	40·14	77·94	6·07	15·99
Takamatsu	4·45	2·63	41·42	51·50	79·52	5·53	14·95
Bibai	3·46	3·86	45·30	47·38	80·27	6·10	13·63
Ashibetsu	2·98	4·05	42·93	50·04	81·11	5·49	13·40
Sunagawa	2·81	2·74	43·36	51·09	81·96	6·12	11·92
Akabira	2·66	2·07	42·15	53·12	82·26	6·26	11·48
Mojiri	2·46	2·80	41·04	53·70	82·51	5·99	11·50
Pocahontas (U.S.A.)	2·09	2·59	43·05	59·27	82·79	6·02	11·19
Futago	1·54	2·31	46·86	49·29	83·16	6·31	10·53
Kamoi	2·13	3·11	41·76	53·00	83·51	6·15	10·34
Yūbari (1)	1·64	3·21	41·11	54·04	83·96	6·21	9·83
Minami-Yūbari	2·18	2·55	39·38	55·89	84·05	6·09	9·86
Miike–Miyanoura	1·10	3·53	44·39	50·98	84·27	5·99	9·74
Heiwa	1·59	2·98	40·68	54·75	84·82	6·23	8·95
Yūbari (2)	1·13	2·67	44·85	51·35	84·85	6·16	8·99
Ōyūbari	1·47	3·74	40·69	54·10	84·89	6·15	8·96
Hashima	1·24	2·09	35·91	60·76	86·59	5·56	7·85
Donegan No. 1 (U.S.A.)	1·75	1·16	31·29	65·80	87·16	5·62	7·22
Kairan (China)	1·24	3·33	31·81	63·62	87·52	5·55	6·93
Doi (Saghalien)	1·45	2·44	20·89	75·22	89·02	5·10	5·88
Shikamachi	1·05	2·47	18·09	78·39	89·47	4·61	5·92
Yatake	1·11	2·74	21·29	74·86	89·55	4·86	5·59
Amonate and Bishop (U.S.A.)	1·06	1·40	23·53	74·01	89·61	5·19	5·20
Itmann (U.S.A.)	1·14	1·14	20·38	77·34	89·74	4·80	5·46
Uonuki	1·68	1·80	10·80	85·72	91·16	3·97	4·87
Sanyō	—	1·76*	—	—	91·47	3·82	4·71
Hongei (Indo-China)	1·92	1·08	6·25	90·75	92·65	3·48	3·87
Kōkō (China)	4·30	2·08	—	—	94·48	1·40	4·12
Ceylon Graphite	—	0·02*	—	—	—	—	—

* Dry basis

After the condition of the measuring apparatus has become stabilized, the meniscus is adjusted to the zero mark of the burette, then the stopcock is closed. The sample in the small glass cup is tipped and dispersed into the oxidizing solution by rotating the glass capillary tube 180° about its axis and by gently shaking the flask. This starts the reaction. The volume of gas evolved is measured by the burette as a function of time under the condition of gentle shaking of the flask every five minutes.

Assuming that all the gas evolved is carbon dioxide, the volume of gas is converted to the state of normal temperature and pressure. Assuming that the fraction decomposed of the carbon content of coal is equal to that of the coal itself, the fraction decomposed of coal is calculated.

Toluene is used as the heating medium and the measured reaction temperature is 109·5°C.

The accuracy of the experiment is better than ± 2 per cent considering the errors of sampling, reading of the burette, and the change of room temperature and atmospheric pressure.

RESULTS AND DISCUSSION

Some experimental results are shown in *Figure 2* where the fraction of coal decomposed is plotted against time. These decomposition curves are classified in the following three types with degree of coalification:

(*1*) the rate is very large initially but becomes suddenly small as decomposition proceeds

(*2*) the decomposition curve is sigmoid but becomes almost linear beyond the inflection point

(*3*) the decomposition curve is sigmoid and the rate becomes small beyond the inflection point.

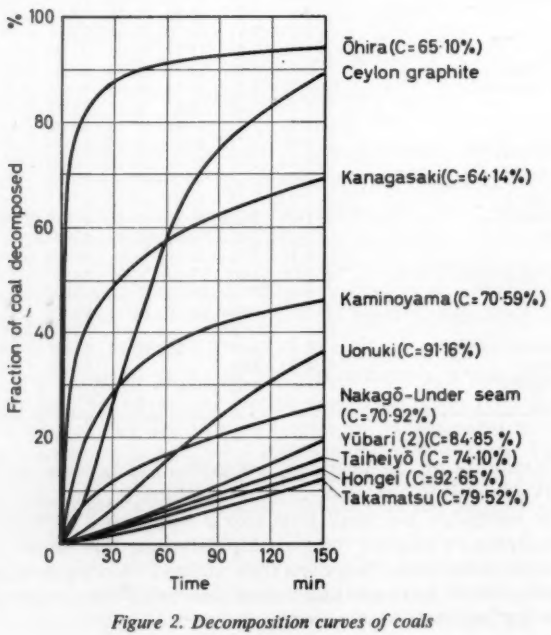


Figure 2. Decomposition curves of coals

Of course there are intermediate curves between these types. Such decomposition curves show the complexity of the reaction mechanism and the large range of reaction mechanisms depending on the degree of coalification.

Paying no regard to the variation of reaction mechanism, the rate of all reactions is approximately represented by the value of the fraction of coal decomposed in a constant time. The relation between the fraction of coal decomposed in 150 minutes and the coal rank is shown in *Table 2* and *Figure 3.*

Table 2. Fraction decomposed of various vitrains

Source	*Carbon (d.a.f.) %*	*Fraction decomposed in 150 min %*	*Source*	*Carbon (d.a.f.) %*	*Fraction decomposed in 150 min %*
Kanagasaki	64·14	69·1	*Minami-Yūbari*	84·05	24·2
Ōhira	65·10	94·0	*Miike-Miyanoura*	84·27	18·9
Tempoku—First seam	68·12	22·3	*Heiwa*	84·82	22·7
Kaminoyama	70·59	45·8	*Yūbari (2)*	84·85	19·0
Nakagō—Under seam	70·92	25·8	*Ōyūbari*	84·89	25·7
Taiheiyō	74·10	15·8	*Hashima*	86·59	20·4
Nakagō	74·33	17·7	*Donegan No. 1 (U.S.A.)*	87·16	26·4
Tsuzura	75·46	15·8	*Kairan (China)*	87·52	26·2
Kashima	77·94	12·1	*Doi (Saghalien)*	89·02	37·6
Takamatsu	79·52	12·1	*Shikamachi*	89·47	32·2
Bibai	80·27	15·4	*Yatake*	89·55	33·5
Ashibetsu	81·11	16·2	*Amonate and Bishop (U.S.A.)*	89·61	31·5
Sunagawa	81·96	20·6			
Akabira	82·26	18·1	*Itmann (U.S.A.)*	89·74	31·2
Mojiri	82·51	22·6	*Uonuki*	91·16	36·0
Pocahontas (U.S.A.)	82·79	18·9	*Sanyō*	91·47	14·8
Futago	83·16	14·8	*Hongei (Indo-China)*	92·65	13·7
Kamoi	83·51	20·3	*Kōkō (China)*	94·48	29·1
Yūbari (1)	83·96	20·8	*Ceylon Graphite*	—	89·1

For lignite, brown coal and non-caking coal the fraction decomposed decreases with rank, and reaches a minimum at about 80 per cent carbon content. For caking coal and coking coal the fraction decomposed increases with rank to a maximum at about 90 per cent carbon content. For anthracite the fraction decomposed decreases again with rank to a minimum at about 93 per cent carbon content; for meta-anthracite and graphite, it suddenly increases again.

The quantity of oxidizing solution is so large compared with that of the sample that the effect of the quantity of oxidizing solution is negligible if the same concentration of oxidizing solution is always used. Therefore the rate of reaction is proportional to the quantity of coal sample only in the first order but the reaction rate should be proportional to the contact surface area of the sample with the oxidizing solution because the reaction is the heterogeneous one between liquid phase and solid phase.

According to H. L. RILEY[1–5] the reaction rate is proportional to the surface area of the sample grain in the geometrical meaning and the large reactivity

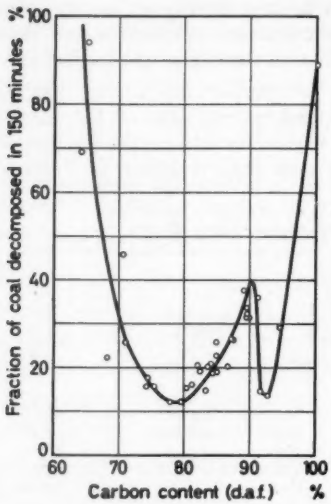


Figure 3. Wet oxidizability as a function of coal rank

of lower rank coal is explained by the large surface area. Therefore the change of the fraction decomposed with rank of coal should be considered from the point of view of specific surface area and the physical condition of the sample.

The relation between the density measured with water at 20°C and rank of coal is shown[7] in *Figure 4*. The density shows a minimum at about 85 per cent carbon content. This result is similar to those obtained by R. E. FRANKLIN[8–9], J. A. DULHUNTY and R. E. PENROSE[10], and D. W. VAN KREVELEN and H. A. G. CHERMIN[11] using helium. *Figure 5* shows the relation between the internal surface area calculated from the adsorption of water vapour and

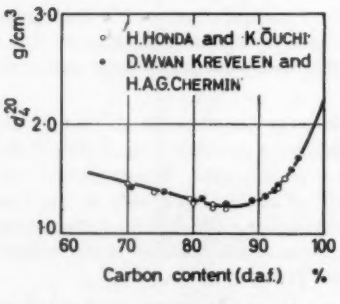


Figure 4. True density as a function of rank of coal (see refs. 7 and 11)

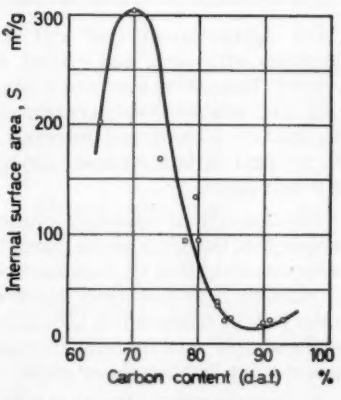


Figure 5. Internal surface area as a function of rank of coal

rank of coal[12]. The internal surface area of coals decreases and then passes through a minimum at about 90 per cent carbon content with increase in rank. This result is similar to the relation between the porosity and rank of coal obtained by J. G. KING and E. T. WILKINS[13]. The heat of wetting also shows a minimum at about 90 per cent carbon content[14]. Though it is almost impossible to measure directly the true contact surface area of the sample and the oxidizing solution which are concerned in the reaction, it may be possible that the true contact surface area is proportional to the accessible

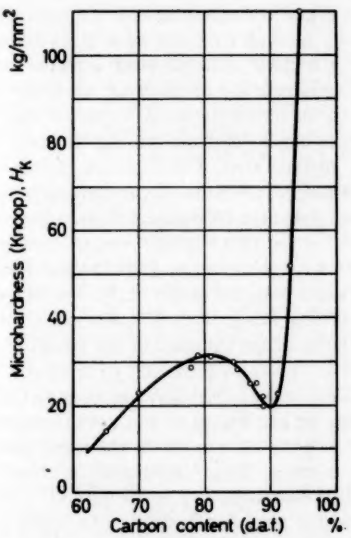


Figure 6. Microhardness number as a function of rank of coal

internal surface area and the porosity of coals measured by the several methods mentioned above, and that the effect of the specific volume is almost negligible.

The fraction decomposed of coals decreases with decrease of internal surface area over the range from about 60 to about 80 per cent carbon content but the former increases with rank over the range from about 80 to about 90 per cent carbon content in spite of the decrease of the latter. This shows that the fraction decomposed of coals is much more affected by the constitution of coals than the internal surface area of coals.

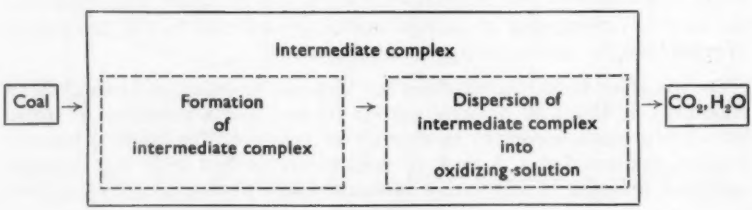
On the other hand, the hardness (or Young's modulus) of coals shows a maximum at about 80 per cent carbon content and a minimum at about 90 per cent carbon content as shown[15] in *Figure 6*. The relation between fraction decomposed and rank of coal coincides well with that between hardness and rank of coal except meta-anthracite beyond about 93 per cent

carbon content. That is to say the fraction decomposed of coals decreases with increase of hardness of coals over the range from about 60 to 80 per cent carbon content, increases with the decrease of hardness of coals over the range of about 80 to 90 per cent carbon content, and decreases again with increase of hardness of coals over the range of about 90 to 93 per cent carbon content. Though the hardness of coals increases beyond about 93 per cent carbon content, the fraction decomposed of coals also increases and approaches the larger fraction decomposed of graphite.

The large wet oxidizability of lignite at about 65 per cent carbon content may be attributed to a kind of cellulose-like (or lignin-like) characteristic of the structure of lignite, such as aromatic base units dispersed in the aliphatic hydrocarbon and oxygen chain, and the large internal surface area of lignite. The decrease of wet oxidizability of coals up to about 80 per cent carbon content is attributed to the development of bridge linkages of aliphatic hydrocarbon, oxygen and carbon to carbon among the coal base units, and the decrease of internal surface area. The increase of wet oxidizability of coals over the range from about 80 to about 90 per cent carbon content is attributed to the destruction and decrease of bridge-linkages and hydrogen bonds, etc. Recent studies of coal show that the number of condensed aromatic rings of the coal base unit is on the average about three to four in the bituminous coals and hardly increases with the rank[7, 16–19]. Therefore the sudden increase of wet oxidizability in this range does not depend upon the spreading of the condensed aromatic rings or the increase of the stacking of the coal base units with rank. The decrease of wet oxidizability of anthracite over the range from about 90 to about 93 per cent carbon content, though the internal surface area increases slightly, may be attributed to the development of cross-linkages of carbon to carbon among the base units. In the meta-anthracite beyond about 93 per cent carbon content, large condensed aromatic rings in stacks are produced, and graphite-like structure is developed. Therefore the oxidizing solution easily penetrates into the graphite-like layer and the wet oxidizability increases suddenly.

In the above discussion, the wet oxidizability of coals is simply compared on the basis of the fraction decomposed in 150 minutes. But the change of wet oxidizability with coal rank is not simple at all from the standpoint of the decomposition curves shown in *Figure 2*. These decomposition curves are classified in types as mentioned above and have a characteristic type for every step of coalification degree. The significance of the curve profile may be considered by analysis of the reaction mechanism.

A complex reaction such as the following may be postulated.



Coal eventually becomes carbon dioxide and water through the several steps of intermediate oxidized products by the mutual action of phosphoric acid and oxidizing agent. Therefore it may be considered that the decomposition curves of many kinds of types as shown in *Figure 2* depend on the balance of the rate of formation and the rate of decomposition of the intermediate oxidized products.

Shigengijutsu-Shikenjo,
Resources Research Institute,
Kawaguchi-Saitama, Japan

(*Received January 1958*)

REFERENCES

[1] BLAYDEN, H. L. and RILEY, H. L. *J. Soc. chem. Ind., Lond.* 54 (1935) 159T
[2] BALFOUR, A. E. and RILEY, H. L. *J. chem. Soc.* (1935) 1723
[3] BALFOUR, A. E., RILEY, H. L. and MORRIS ROBINSON, R. *J. chem. Soc.* (1936) 456
[4] BALFOUR, A. E., BLAYDEN, H. E., CHARTER, A. H. and RILEY, H. L. *J. Soc. chem. Ind., Lond.* 57 (1938) 1
[5] RILEY, H. L. *Trans. Faraday Soc.* 34 (1938) 1011
[6] AKAMATSU, H., TAKAHASHI, H. and TAMARU, K. *Bull. chem. Soc. Japan* 24 (1951) 27
[7] HONDA, H. and ŌUCHI, K. *Fuel, Lond.* 36 (1957) 159
[8] FRANKLIN, R. E. *Fuel, Lond.* 27 (1948) 46
[9] FRANKLIN, R. E. *Trans. Faraday Soc.* 45 (1949) 274
[10] DULHUNTY, J. A. and PENROSE, R. E. *Fuel, Lond.* 30 (1951) 203
[11] VAN KREVELEN, D. W. and CHERMIN, H. A. G. *Fuel, Lond.* 33 (1954) 79
[12] KAWANA, Y. *Report* of the Annual Meeting of Coal Science, Japan, 1955
[13] KING, J. G. and WILKINS, E. T. *Proc. Conf. Ultrafine Structure of Coals and Cokes*, p 46. British Coal Utilisation Research Association: London, 1944
[14] GRIFFITH, M. and HIRST, W. *Proc. Conf. Ultrafine Structure of Coals and Cokes*, p 80. British Coal Utilisation Research Association: London, 1944
[15] HONDA, H. and SANADA, Y. *Fuel, Lond.* 36 (1957) 403
[16] NELSON, J. B. *Fuel, Lond.* 33 (1954) 381
[17] HIRSCH, P. B. *Proc. Roy. Soc. A* 226 (1954) 143
[18] BROWN, J. K. and HIRSCH, P. B. *Nature, Lond.* 175 (1955) 229
[19] DRYDEN, I. G. C. *J. Inst. Fuel* 30 (1957) 193

Recent Developments and Notes

COKE SIZE AND CUPOLA PERFORMANCE

In order to investigate the effect of size of coke on cupola performance the British Coke Research Association has conducted trials at the Nutbrook Plant of the Stanton Ironworks Company Limited and an interim report to the Research Committee has now been published [*B.C.R.A., Panel No. 10, The effects of coke size on cupola performance*, September 1957].

Three size-ranges of a good quality Welsh foundry coke were tested on a continuously tapped, cold-blast cupola of internal diameter 46 in., operating with a metal/fixed carbon ratio of 14:1 (metal/coke ratio, 12·5:1) and a mean air rate of 3 300 ft³/min. It was found that alteration of the coke size from 1 to 3 in. to 3 to 5 in. caused changes in the cupola performance, but that there was no significant difference between the performances with 3 to 5 in. and coke originally sized above 5 in. The best cupola performance was obtained with both 3 to 5 in. and above 5 in. sizes. The temperature of the molten metal for these sizes was 1 425°C as compared with 1 379°C for the 1 to 3 in. coke. Compared with the two grades of larger size and the ungraded coke, the 1 to 3 in. grade was characterized by a higher melting rate for a standard blast volume, a slower rate of temperature recovery after off-blast periods and a lower efficiency of coke combustion. There were no significant changes in metal quality or heat efficiency which could be attributed to the effect of coke size.

ISOMERIZATION OF NAPHTHAS

A new process for the isomerization of naphthas has been announced by Société Kellogg, Paris, which is a subsidiary of M. W. Kellogg Co., New York [*Chim. et Industr.* 78 (1957) 561]. The process will enable refineries to increase the total production of petrol of high octane number by improving the octane number of combined fractions of pentane and hexane, as well as of natural gasoline.

Improvement in the octane number requires the isomerization of the pentanes and either isomerization or reforming of the hexanes. As the latter are difficult to reform to aromatics, it is better on economic grounds to carry out isomerization of the combined pentanes and hexanes in a single unit. The vapour-phase ISO–KEL process depends on the use of a new catalyst containing a precious metal, not platinum, in a single reactor in the presence of hydrogen. Two separate products are obtained, *iso*pentane with an octane number of 105 CFRR and *iso*hexane with a value varying from 89 to 92 CFRR according to the nature of the charge used; in both cases the octane number values are for 3 cm³ of tetraethyl lead added.

COAL SCIENCE

The papers presented to the Second International Conference on Coal Science, held at Valkenburg, The Netherlands, during 1 to 4 May 1957,

have now been published, together with the discussions, in a special number of *BrennstChennie* [39 (February 1958) *Sonderausgabe*]. The papers are divided into four sections: (*i*) chemical methods in the study of coal, (*ii*) new physical techniques in the study of coal, (*iii*) physicochemical studies of the macerals, and (*iv*) fundamental studies in the carbonization of coal.

REFRACTORIES RESEARCH

New information on the character of scurf revealed by a study of its microstructure is given in a paper presented to the Autumn Research Meeting of the Institution of Gas Engineers in November last, by E. W. ROBERTS [*Gas Counc. Res. Commun. No. GC 39* (1957)]. This paper and others presented at the same meeting describe investigations carried out for the Gas Council by the staff of the British Ceramic Research Association under its Director, A. T. GREEN, C.B.E. Scurf has usually been regarded as an amorphous form of carbon, but it is now shown to have a certain amount of organized structure. An attempt is made to account for its structure in the light of recent researches on forms of carbon by other workers. Further knowledge of the microstructure of scurf may be expected to assist in accounting for the association between the presence of scurf and flaking of refractories in continuous vertical retorts.

Another paper presented to the meeting, by J. F. CLEMENTS and J. VYSE, gives further information on the sonic spalling test. This test for detecting cracking due to thermal shock consists essentially of observing changes in the resonant frequency of a test piece while it is being heated. The paper gives an account of the search for a method of measuring the damage done by a spalling crack. No generally applicable method has yet been found but some interesting observations have been made. It appears that sensitivity to thermal shock is separable into two components, the tendency to crack and the tendency to break as a result of the crack. These properties seem to be mutually independent and neither can be clearly related to porosity or mechanical strength. This is an unusual view of spalling.

METHODS FOR TESTING TAR PRODUCTS

The fourth edition of *Standard Methods for Testing Tar and its Products* has recently been issued and is a thorough revision of the 1950 edition (Standardization of Tar Products Tests Committee: Oxford Road, Gomersal, near Leeds, 1957). There are thirteen new methods, eleven tentative methods and three tentative methods have been adopted as standard methods. There are over 100 pages more than in the previous edition and there is a much expanded index.

NEW GILSONITE REFINERY

A new plant of the American Gilsonite Co. at Gilsonite, Colorado, is now producing conventional petroleum products from the non-petroleum material, gilsonite [*Gas World* 147 (1958) 304]. High grade coke and high-octane petrol are the important products of the plant which is one of the larger

delayed coking units in the U.S.A. The gilsonite is delivered in water to the refinery in Colorado, by means of a 72-mile pipeline from Bonanza, Utah.

Before entering the coking furnace which operates at 485°C the gilsonite is passed through a filter plant and to a melting tank where it is heated to about 230°C. From the coker the green coke passes to a calcining plant, and the hot waste gas from the calciner is burned in boilers to generate steam. From the delayed coker the raw petrol passes via a coker gas recovery section to the catalytic reformer. This consists of three sections, one for the generation of hydrogen which is pumped into the raw petrol in the second section of the reformer. This brings about the removal of nitrogen, which would render the catalyst non-effective, before the raw petrol passes to the final section where the catalytic reforming takes place by means of the 'platforming' process.

SILICA–ALUMINA CATALYSTS

One of the most important physical properties of a cracking catalyst as used in the petroleum industry is its specific surface area. The surface area of a porous catalyst, such as silica–alumina, is almost entirely composed of the surface of pores in each catalyst particle. The diameter of the pores may vary from a few to a few hundred Ångström units. The accessibility of the surface to reactants depends on the relative proportions of pores of different sizes. In order to assess the relative effectiveness of different porous catalysts reliable values for the average pore size are required. In an attempt to obtain such values J. H. RAMSER and P. B. HILL, of the Research and Development Dept, The Atlantic Refining Co., Philadelphia, have recently used the capillary condensation method to obtain adsorption and desorption isotherms, and thence obtained by calculation the pore size and surface area distributions of 31 fresh and sintered silica–alumina catalysts [*Industr. Engng Chem.* (*Industr.*) 50 (1958) 117]. Nitrogen was used and its adsorption was measured under reproducible conditions of near-equilibrium. It was found that the average pore radius, as calculated from actual pore size distribution curves, is only about half as large as the average radius estimated from pore volume and surface area as frequently given in the literature. The discrepancy between estimated and true average pore radius depends on the width of the pore size distribution as measured by its standard deviation. Close correlation between the standard deviation and the ratio of pore volume to surface area may be used to estimate true average pore radius.

OIL AND NATURAL GAS IN EUROPE

The Commission for Energy of the Organisation for European Economic Cooperation (OEEC) completed its work in 1956 with the issue of a report *Europe's growing needs of energy, how can they be met?* and in the same year the Oil Committee expressed an opinion on the future oil situation of Europe in a report *Oil, the outlook for Europe*. Both these reports give estimates of the total needs of primary energy in Western Europe and of oil in particular for 1960 and 1975. It is clearly indicated in both reports that Europe will become more and more dependent on imported oil and that the burden of finding the foreign currency needed to cover the corresponding payments will

constantly increase. The conclusion was that every possible means should be used to discover and exploit new crude oil and natural gas fields on European territory. A study, therefore, has been made by the Oil Committee of OEEC to find out to what extent Western European deposits can make a decisive contribution to the constantly growing demand for hydrocarbons. The findings of the Committee have been published in a report *The search for and exploitation of crude oil and natural gas in the OEEC area* [Organisation for European Economic Cooperation: Paris, 1957].

The present position in oil prospecting is described with regard to the following points: (*i*) mining law and fiscal regulations relating to hydrocarbons, (*ii*) oil geology, (*iii*) discoveries of oil and gas classified geographically and geologically, (*iv*) estimated classification of the various regions in the OEEC area having regard to their oil prospects, (*v*) statistics for past years and up to the end of 1956 for the various aspects of prospecting and exploitation.

It is concluded that there is justification for considerable optimism with regard to the possibility of new oilfields being opened up in OEEC countries. Recent American investigations have shown that even a low bitumen content in marine or brackish deposits, or under favourable circumstances even in fresh-water deposits, suffices to indicate oil accumulations which are economically exploitable. In view of the proved existence of such sediment basins on a large scale in OEEC countries [Austria, Belgium, Denmark, France, Germany (Fed. Rep.), Greece, Ireland, Iceland, Italy, Luxembourg, Netherlands, Norway, Portugal, Sweden, Switzerland, United Kingdom (and Spain and Yugoslavia, non-member countries)] and the fact that the exploration carried out up to the present is far from adequate, it may therefore be expected that new oil and gas occurrences will be found in these basins in the future. About 37 per cent of the total area of these countries has sedimentary basins with either rather favourable or favourable prospects. On the whole Western Europe can be considered to have distinctly encouraging oil prospects owing to the size of the favourable sedimentary basins, the existence of large deposits in the most varied regions and in formations belonging to different geological periods, the rapid increase in production in the last ten years and the high percentage of successful exploratory borings.

RUSSIAN CLASSIFICATION OF COKING COALS

A classification for coals, described by N. I. TURCHENEV, has been worked out on a new basis from data on coals from the East Fergana, Donets, Pechora and Kuznetsk coalfields [*Trud. Lab. Geol. Uglaya* (*Proc. Lab. Geol. Coal, Acad. Sci. U.S.S.R.*) 6 (1956) 112]. The parameters used are: (*i*) the total amount of gelled matter (*EG*) and cutinized elements (*K*) in relation to the total mass of the coal, (*ii*) the thickness of the plastic layer (*y*), (*iii*) $y/(EG + K)$, which indicates the chemical maturity of the gelled matter. The classification diagram consists of a right-angled triangle and its mirror image, with $(EG + K)$ as the abscissae axes and y as the ordinate axes. Straight lines joining points corresponding to particular values of y with the apex of the triangle, which corresponds with zero value of abscissae, form angles α with the abscissae axis. The third derived parameter of the classification is $\tan \alpha = y/(EG + K)$. The classification reflects the relationship of

the coking power of the coals with their composition and chemical maturity, which is connected with the initial reducibility of the coal-forming matter and its further transformation during metamorphism.

PETROLEUM CONGRESS

The Fifth World Petroleum Congress is to be held in the Coliseum, New York City, in early June 1959. The subjects to be discussed were recently considered at a meeting in Germany of the Permanent Council of the World Petroleum Congress, presided over by E. V. MURPHREE, chairman of the Council and president of Esso Research and Engineering Co. A highlight of the Congress will be a symposium on the exploratory use of atomic energy for new methods of processing oil and for creating new products. Amongst other key subjects for discussion are searching and drilling in off-shore regions, new techniques for recovering more oil from oilfields, petrochemicals for making new plastics and synthetic fibres, new refining methods designed to contribute to oil conservation, relationship of fuel requirements of free-piston and gas turbine engines to the types of petroleum products needed in different areas of world, new techniques for removing sulphur from petroleum, international standardization of methods for inspection and evaluation of petroleum products.

Enquiries should be addressed to: The Secretary, British National Committee, World Petroleum Congress, 26 Portland Place, London, W.1.

SHELL GASIFICATION PROCESS

The first industrial Shell gasification plant was put into commission at IJmuiden, Netherlands, in December 1956 and a similar plant is now being constructed at the Shell Refinery in Shellhaven. This plant will have a throughput of 200 tons of heavy fuel oil per day and will provide gas for the manufacture of synthetic nitrogen fertilizers.

The process is based on the continuous, non-catalytic partial oxidation of liquid or gaseous hydrocarbons to produce a gas with a high content of hydrogen and carbon monoxide suitable as a synthesis gas and in the production of town gas. The process uses oxygen or oxygen-enriched air and operates at high pressure. A wide range of feedstocks can be gasified.

COLLOIDAL CHARACTERISTICS OF PETROLEUM

The presence of discrete colloidal particles in three crude petroleums from the Illinois basin has been definitely established by sedimentation studies. These have been described by B. R. RAY, P. A. WITHERSPOON and R. G. GRIM [*J. phys. Chem.* 61 (1957) 1296]. Centrifugation at 80000 *g* at room temperature and for periods up to 12 days demonstrated that different groups of colloidal materials are dispersed in the oils. Extensive work on one oil yielded four fractions, one being a black organic sediment, two contained red and black coloured particles, and a very small fourth fraction consisted of inorganic colloidal matter, mostly fine clay. The top layer of oil became a yellow-green translucent fluid of decreased viscosity and density. The sediments, up to 2 per cent of the total oil in one case, were characterized by analytical sedimentation as consisting of particles of average molecular

weight 30000, diameter 40 Å, and density 1·22. Elemental analysis of the sediments confirmed their asphaltene character; nickel and vanadium were concentrated 25- to 30-fold in the sediments. The results support the view that petroleum and asphalts possess a micellar structure in which dense asphaltenes act as nuclei and are surrounded by less dense maltenes.

SECOND GENEVA ATOM CONFERENCE

In July last year it was announced that the British Government had accepted an invitation from the Secretary-General of the United Nations to participate in a second International Conference on the Peaceful Uses of Atomic Energy, from 1 to 13 September 1958.

The provisional agenda agreed by the seven-nation Advisory Committee covers all aspects of the peaceful applications of atomic energy. The President of the Conference is to be Professor F. PERRIN, of the Commissariat à l'Energie Atomique de France and the Secretary-General, Dr S. EKLUND, of Sweden.

Arrangements for the United Kingdom's participation are being organized by an Executive Committee of which the Chairman is Sir JOHN COCKCROFT and the Secretary, B. W. MOTT.

The Papers Committee has considered the suitability of a large number of suggested papers and has selected about 200 for submission to the United Nations. This represents about 10 per cent of the total number expected from all participating countries. Two atomic energy exhibitions will be held in Geneva during the Conference.

The U.K. delegation is expected to consist of five delegates, about 250 advisers and about 250 observers, the advisers being drawn primarily from among the authors of papers. The leader of the U.K. delegation will be Sir JOHN COCKCROFT, Member for Scientific Research of the United Kingdom Atomic Energy Authority. The other four delegates are expected to be a second representative of the Authority and representatives of the Royal Society, British industry, and the Medical Research Council.

RINGELMANN CHART

The method of visual assessment of smoke emission by comparison of the darkness of the smoke with standard shades of grey on a chart placed in a suitable position was devised by Professor RINGELMANN of Paris towards the end of last century. The shades of grey were obtained by cross-hatching in black on a white background so that a known percentage of the white was obscured. In use the charts were placed at such a distance from the observer that the black lines merged into the white background and produced for each shade, apparently, a uniform shade. The numbers of the shades—Ringelmann Numbers—range from 0—white to 5—black, the stages being by changes of 20 per cent in obscuration of the background. The Ringelmann Chart is the basis of assessing conformity with legislation in the Clean Air Act which became fully effective on 1 June 1958. The Act forbids pollution of the air by *dark smoke*, which is defined as smoke as dark or darker than shade 2 on the Ringelmann Chart.

A *B.S. 2742 C:* 1957 has recently been issued in which the chart has been so printed as to reproduce with consistency shades of grey which are near the average of the commercially printed charts in general use, from which acceptable measurements of smoke are produced. In addition to this, a separate publication 'Notes on the use of the Ringelmann Chart' (*B.S. 2742:* 1958) has been issued.

There are other *British Standards*, dealing with the manufacture and use of smoke alarms and indicators, which are of interest to those concerned with the implementation of some of the provisions of the Clean Air Act. In particular there are: *B.S. 2740:* 1956—'Simple smoke alarms and alarm metering devices'; *B.S. 2741:* 1957—'Simple smoke viewers'; *B.S. 2811:* 1957—'Smoke density indicators and recorders'.

CHEMICAL REACTION ENGINEERING

At the twelfth meeting of the European Federation of Chemical Engineering, organized by Het Koninklijk Institut van Ingenieurs and held in Amsterdam on 7 to 9 May 1957, the first European Symposium on 'Chemical reaction engineering' was held. The chairman of the Symposium Committee was Dr Ir J. C. VLUGTER. The main theme was the relation and interaction of flow phenomena, mass and heat transfer, and reaction kinetics and the influence of these factors on successful reactor design. Fifteen papers were presented and these have recently been published [*Chem. Engng Sci.* 8 (1958) 1 to 200].

NEW COAL BIN DISCHARGE SYSTEM

The first full scale tests of the Easy-Flo Bin, devised by Bituminous Coal Research Inc., have proved highly successful [*Bituminous Coal Research*, No. 18 (No. 1) (1958) 7]. A 45-ton capacity silo was loaded both at a continuous rate of half a ton per minute, and by 1-ton free-falling increments severe enough to produce pressures exceeding those in normal silos and bunkers. The new bin handled coal loaded by both methods equally well.

The essential feature of the new flow system for the discharge of solids from bins is the insertion of a double-cone plug in the bin hopper, directly above the outlet. In the optimum plug shape for coal the cap cone slopes at 77° for a 75° sloped hopper. The effect of the plug is to cause the coal as it leaves the hopper to slip through the annular space between the plug and the hopper walls. In this way the compacted central core of coal which causes poor discharge from a bin is eliminated; ratholes, high pressures and adhesion to the hopper walls are avoided, and there is free movement of coal without jamming. The new bin handles satisfactorily $\frac{1}{4} \times 0$-in. coal with up to 15 per cent of surface moisture and gives reliable flow with sizes up to 3 in.

THE FOXWELL MEMORIAL AWARD

To commemorate the outstanding services to the Institute of Fuel and to the profession rendered by the late Dr G. E. FOXWELL, C.B.E., a Past-President and at the time of his death, Honorary Secretary of the Institute, the Council has established a Memorial Award to be known by his name.

A memorial fund has been set up and apart from a small proportion to provide a memorial tablet at Institute Headquarters, the bulk of the money will be invested to endow an exhibition, scholarship or fellowship to be known by Dr Foxwell's name. The Universities of Leeds and Sheffield will be invited to nominate alternate holders of the award who must be students in Fuel Technology at either undergraduate or postgraduate level in one of these Universities.

BROWN COAL COKE

It was announced by the Gas and Fuel Corporation, Victoria, Australia, that the production of hard coke made from brown coal was to begin in May this year [see *Fuel, Lond.* 37 (1958) 88]. This new fuel has been specially developed for smelting iron and steel and other metals in foundries. It is the result of research for several years in the University of Melbourne. It is predicted that within a few years the brown coal coke will make Victoria independent of the more costly hard coal coke from New South Wales. As the new coke is excellent for the smelting of high grade steel it is expected that it will lead to the establishment of further new industries from Britain and America in the Latrobe Valley area of Victoria which is rich in brown coal.

CANADIAN SECTIONAL MEETING OF THE WORLD POWER CONFERENCE

The Canadian Sectional Meeting of the World Power Conference will be held in Montreal from 7 to 11 September 1958. The theme of the meeting will be 'Economic trends in the production, transportation and utilization of fuel and energy'. The General Programme issued by the Canadian National Committee can be obtained from the Secretary, British National Committee of the World Power Conference, 201-2 Grand Buildings, Trafalgar Square, London, W.C.2.

SOVIET TRENDS IN PHYSICAL MEASUREMENT

The sixth Five Year Plan in the U.S.S.R. which began in 1956 has for its objective the increase of the means of production by 70 per cent and the output of consumer goods by 60 per cent. As part of this programme there is a large scale plan for the adoption of automatic control and regulation of technological processes in industry and to this end part of the plan is concerned with assuring uniformity and accuracy in the methods of physical measurements. Some interesting information about the extensive programme in the techniques of measurement was given recently by A. V. ASTIN, Director of the National Bureau of Standards, Washington, D.C. [*Chem. Engng Progr.* 54, No. 4 (1958) 8].

The development and production of instruments and their effective use are under the direction of the Committee on Standards, Measures and Measurement Apparatus of the Council of Ministers of the U.S.S.R. Five research institutions work under the direction of this Committee and these control a network of calibration centres. By 1960 it is hoped that there will be 129 such centres.

In the field of temperature-measuring instruments it is claimed that already in Russia calibrations up to 6000°C can be made and the Five Year Plan calls for extending this up to 14000°C by 1960. Dr Astin points out that at the National Bureau of Standards satisfactory means for temperature calibration are available only up to 2800°C, and on occasion up to 4200°C by impromptu means. There is a lack of means of producing higher temperatures, the best high temperature-producing device in the Bureau is a small solar furnace capable of attaining temperatures of about 3500°C.

FUEL CONGRESS IN CZECHOSLOVAKIA

The First National Congress of Fuel Technologists was held from 12 to 17 May 1958 at Karlovy Vary, Czechoslovakia. It was organized by the Scientific and Technical Society for the Use of Fuels of the Czechoslovak Academy of Sciences. The president of the Society, Prof. Dr Ing. RUDOLF RIEDL, gave the inaugural address. The various sections of the congress dealt with: coke and gas manufacture, chemicals from coal and oil, combustion and heating, lignite and its use. 140 communications were presented to the congress and the sessions were devoted to discussion of these. Nearly half the communications were from other countries, including Austria, France, Germany, Hungary, Poland, Russia and Yugoslavia.

C.E.G.B. GIANT CAPACITY BOILER

The 550 MW power station boiler, designed by International Combustion Ltd for the Central Electricity Generating Board's Thorpe Marsh Power Station at Doncaster, will have as far as is known a capacity greater than any single unit under project in the world.

By comparison with a 60 MW boiler unit, the largest being installed ten years ago in Great Britain, the new unit will occupy about half the space that would be necessary for a series of 60 MW units with a comparable aggregate capacity. The use of improved combustion chamber design, assisted circulation, and increased capacity pulverizers, will lead to a capital cost that is about 65 per cent of that which would have been involved with smaller units ten years ago. This boiler unit will feed two cross-compounded 275 MW turbo-alternators, and will have an output greater than any of the C.E.G.B.'s existing power stations. It will take three years for the factory assembly to be completed, and the unit is expected to be in operation by 1963. The components for a 275 MW set represent the maximum loads which can be transported from factory to site.

About 2·5 million tons of coal annually will be required ultimately for this power station, and it will be small coal, drawn from a wide area, and consequently its characteristics will vary over a wide range, 6 to 30 per cent of ash, moisture 4 to 20 per cent. The evaporation rate will be 1700 tons per hour. A thermal efficiency of 90 per cent is guaranteed and the unit is designed to operate for twelve months without interruption.

POLISH RESEARCH ON COKING

A conference on coking problems was held from 26 to 30 October 1957, in Katowice, presided over by S. ROSINSKI, Director of the Institute for the

Chemical Treatment of Coal. The eighteen papers presented to the Conference have now been published (*Koks-Smola-Gaz* 2 (1957) 209 to 318). Three of the papers deal with stamping the coal charge for coke production, and its use in Polish coking plants appears to be well justified. In coking the coals from the eastern districts of the U.S.S.R., however, stamping does not invariably effect an improvement in coke quality. The simultaneous use of a high degree of fineness of the coal charge and strong stamping can be disadvantageous.

Two papers relate experimental work in connection with obtaining preformed metallurgical coke made from brown coal, weakly caking or non-caking bituminous coal. One of these papers is by N. R. KUSZNIERIEWICZ, of the U.S.S.R., and the other by L. JAKO, P. TAKACS and K. VOSZATKO, of Hungary (*loc. cit.* pp 294, 299). The technique here used for obtaining preformed coke was due originally to L. M. SAPOZNIKOW [*2nd Coal Geol. Conf., Leningrad, 1955; Trud. Lab. Geol. Uglaya* (*Proc. Lab. Geol. Coal, Acad. Sci. U.S.S.R.* 6 (1956) 137]. The coal is heated as quickly as possible until it attains the plastic state. It is then subjected to a light pressure in a helical press to form a monolith which is heated fairly rapidly to ensure caking, and finally heated slowly to prevent the formation of fissures. The pre-formed coke has high mechanical strength.

NEW PROCESS FOR MAKING TOWN GAS

A new method of gas production is to be used in a £2 million plant at Partington, near Manchester, to be erected under the authority of the North Western Gas Board. It will be engineered and built by Humphreys and Glasgow, Ltd, and is planned to be in operation at the beginning 1960. Advantages of the new method are expected to be cheapness, flexibility in raw materials, low toxicity of the gas, freedom from sulphur compounds and availability at high pressure. The high pressure will allow the gas to be transmitted economically over long distances without compression, so that the production plants can be sited where raw materials are cheapest.

The new process produces gas in an automatically controlled plant by the hydrogenation of oil or coal and is due to the investigations carried out by Dr F. J. DENT, Director of the Gas Council's Midlands Research Station at Solihull. A wide variety of different grades of oil can be used, taking advantage of fluctuations in the price of oil refinery byproducts. Later it is intended that low grade coal will take the place of oil. The installation at Partington will have a capacity of 7·5 million ft^3 of gas per day. Gas made in this demonstration plant will cost about the same as gas produced by conventional methods, but for bigger plants considerable reductions in both capital and operating expenditure would reduce costs considerably.

The gasification system of the new plant will comprise the production and purification of hydrogen in excess of 90 per cent purity by the gasification of oil at a pressure of 400 lb/in^2 with oxygen and steam, and the use of this hydrogen for the production of rich gas by hydrogenating further oil to produce gas with a calorific value of about 600 B.Th.U./ft^3.

The process used for the production of hydrogen is that of the Texaco Development Corpn. The gas produced by this process is a mixture of carbon

monoxide and hydrogen and the proportion of hydrogen in the gas is increased by a catalytic conversion plant. The purification of the hydrogen is carried out by the Benfield process of absorption in potassium carbonate solution.

The purified hydrogen is preheated and fed into the hydrogenator together with preheated oil which is converted at high temperature essentially to methane, together with a proportion of ethane. The gases leaving the hydrogenator contain benzene and other aromatic compounds which are removed by condensation and scrubbing with circulating oil. The resultant gas, free of benzene, is then diluted with nitrogen to bring the gas to the required calorific value and density.

In this system both the specific gravity and the carbon monoxide content of the gas are under control; it is intended that the content of the latter should be at least as low as one per cent, thus greatly reducing the toxicity of the gas. The organic sulphur content of the gas is also very low.

LURGI PLANT TO BE BUILT IN SCOTLAND

It was announced recently that a new gas plant is to be built for the Scottish Gas Board, at Westfield, in Fife, at a cost of £6·5 million. It will use the Lurgi high-pressure complete-gasification process and it will be the first time this process has been used in Britain. Low grade opencast coal will be fed directly to the plant by conveyor belt from a National Coal Board site which is said to have sufficient reserves of opencast coal to meet the requirements of the plant for 20 years when on full production of 30 million ft³ of gas per day. Conventional plant of the same capacity would cost at least £1 million more than the Westfield scheme. There will be an interim stage in the construction of the plant, for an output of 15 million ft³ per day and this is expected to be completed by July 1960. The second stage is to be completed by September 1962.

The coal will be completely gasified in the Lurgi generators at 25 atm pressure in a continuous stream of oxygen and superheated steam. The crude gas leaving the generators will have a calorific value of about 300 B.Th.U./ft³. The proportion of hydrogen in the Lurgi gas will be increased by the use of iron oxide catalyst in a conversion plant, at high pressure and temperature. After purification by the Benfield process, the calorific value will be 400 B.Th.U./ft³ and subsequent enrichment by the oil hydrogenation process, similar to that to be used in the new plant at Partington, Lancashire (see previous note), will raise the calorific value to 700 B.Th.U./ft³. Dilution with nitrogen before distribution will reduce the calorific value to the normal value for town gas, 450 B.Th.U./ft³.

NEW SHELL ALKYLATION PLANT

A plant to manufacture alkylate as a component of aviation gasoline was recently started up at Shell's Pernis Refinery, Rotterdam. This refinery is now in a position to produce aviation gasoline, which previously had to be imported. The alkylation plant is the first of its kind in Western Europe.

The production of alkylate depends on reaction between butene and *iso*-butane which are both produced in ample quantities by the refinery's two

catalytic cracking plants. The hydrocarbons are first liquefied under pressure, purified, and then brought into contact with hydrofluoric acid to form alkylate.

TRANSPORT OF LIQUID NATURAL GAS

It was announced recently that a contract has been signed between the Gas Council and Constock Liquid Methane Corpn of America for the experimental importation into Great Britain of liquefied natural gas by sea. A cargo ship, jointly owned by the Gas Council and the Corporation, is being converted and will be able to carry about 2000 tons of liquid natural gas. It is hoped that that the first shipload will arrive in the Thames by about the end of 1958.

If this experiment proves successful it is hoped that, subject to Government sanction, the importation of liquefied natural gas in bulk will be possible. The principal constituent of natural gas, methane, requires a temperature of − 260°F for liquefaction at atmospheric pressure and volume of the liquid is 1/600 of that of the gas.

It is proposed to take the first trial loads of natural gas from the Gulf Coast oilfields. For the trial shipment it is intended to use an already existing liquefaction plant which has been constructed on a barge, and can be transported to any site in the area at which the natural gas may be loaded. The liquid methane will be contained in five tanks insulated with balsa wood and their overall design and location will be such as to accommodate the effect of ship's movement at sea. As the liquid methane cargo is exceptionally light the ship will be specially ballasted.

The marine terminal for the acceptance of the trial shipment in this country will be at Canvey Island on land belonging to the North Thames Gas Board and where there are suitable deep water facilities. The Board is undertaking special constructional work to receive the liquid methane and the two storage tanks necessary to deal with the trial shipment are now under construction.

The liquid methane will be converted to gas under pressure and this pressure will be used to convey the gaseous methane into the Board's transmission lines. A new transmission line is being laid from Canvey Island to connect with a high pressure main already in existence between Shellhaven and Romford Works and the gaseous methane will mix with refinery gases from the Shellhaven refinery.

THERMAL INSULATION OF INDUSTRIAL BUILDINGS

Proposals for regulations to be made under the Thermal Insulation (Industrial Buildings) Act, 1957, are contained in a memorandum which has been circulated to organizations interested in the subject by the Ministry of Power.

The main purpose of the Act which became law in July 1957 is to prevent the unnecessary waste of fuel that occurs as a result of inadequately insulated buildings. The Act applies only to new factories started on or after 1 January 1959, unless the Minister of Power appoints an earlier date, but it is hoped that the insulation of these buildings will encourage the owners of existing factories, commercial buildings and houses to follow suit.

The Act itself does not lay down any standard of insulation but provides for the Minister to make regulations prescribing a standard and dealing with other related matters. During the passage of the Bill through Parliament, the Minister undertook to consult organizations who might have an interest in the effect of the Regulations, before he reached a final decision on their contents. This consultation is now taking place and proposals for the contents of the Regulations have been summarized in a memorandum (*Ministry of Power, Reference EF, 63/5/16*), on which interested organizations are being asked to comment.

GAS COUNCIL MIDLANDS RESEARCH STATION

The Midlands Research Station of the Gas Council at Solihull, Warwickshire, was officially opened on 1 April by Sir CYRIL HINSHELWOOD, President of the Royal Society. The work of the station is largely directed to the investigation of processes for the complete gasification of low grade coals, hitherto considered unsuitable for gas making.

The processes which are being investigated include the gasification of coal using Lurgi gasifiers, slagging gasifiers, and fluidized coal. Whilst the two former processes require a proportion of the coal to be above $\frac{1}{4}$ in. size, the fluidized process will deal with any size of coal down to dust. It incorporates the hydrogenation of the coal itself and it is thought to be the best method both for byproduct recovery and gas enrichment. The process has reached the pilot scale of development. It will have an overall thermal efficiency of 75 per cent.

Other processes which are being studied are the pressure gasification of oil, either for crude and heavy oil or for distillates, and the pressure catalytic process for light distillate oils, which has been specially developed for peak load purposes.

There is also utilization research on high velocity jet burners, recuperation of heat by plate type heat exchangers, flame traps, explosion relief for industrial ovens, a portable suction pyrometer, and refractories of low thermal conductivity.

DIFFERENTIAL THERMAL ANALYSIS

A new procedure for carrying out differential thermal analysis has been described by D. D. WILLIAMS, R. D. BAREFOOT and R. R. MILLER, of the U.S. Naval Research Laboratory, Washington, D.C. [*Analyt. Chem.* 30 (1958) 492]. In contrast to the usual method of heating a furnace through a temperature range at a constant rate, in this method a vertical heavy-walled metal tube 32 in. long is used to establish a constant reproducible temperature gradient. The sample holder, containing the base and differential thermocouples, is pulled through the tube at the rate required to produce the desired rate of temperature change.

SEVENTH INTERNATIONAL SYMPOSIUM ON COMBUSTION, 1958 LONDON AND OXFORD

The attention of readers of *Fuel* is drawn to the Seventh International Symposium on Combustion which will take place in London and Oxford (England) from 27 August to 3 September. The theme of the Symposium will

be 'The Physics and Chemistry of Flames'. Full information may be obtained from the Chairman, The Combustion Institute Committee, c/o The Institute of Fuel, 18 Devonshire Street, Portland Place, London, W.1.

ACS GAS AND FUEL CHEMISTRY MEETING

A special spring meeting of the Gas and Fuel Chemistry Division of the American Chemical Society was held from 15 to 16 May 1958 at the Illinois State Geological Survey, Urbana, Ill. Eleven papers were presented to the meeting and two of these relate to research on the constitution of coal.

B. GREIFER, formerly of the Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, described an apparatus for the vacuum pyrolysis of bituminous coal. The furnace was designed to be operated at initial pressures as low as 10^{-4} mm of mercury, to decrease the sample-to-condenser distance, and to achieve a more reliable control of temperature than hitherto. The vacuum pyrolysis of coal under these conditions can be regarded as achieving a gentle degradation which gives rise to little secondary cracking. This is substantiated by, amongst other things, the close similarity between the infra-red absorption spectrum of the original coal and that of the solid condensate. Hence the solid condensate is concluded as representing primary decomposition products which have a close resemblance to the parent coal. The product which condensed at tap-water temperature was a solid, reddish-brown, enamel-like deposit, not semi-solid or liquid as obtained by previous investigators. The pyrolysis temperatures in the different experiments ranged from about 350° to 530°C.

An examination of the solid condensate was made by means of infra-red and ultra-violet absorption spectra, molecular weight, molar refraction, solubility, and softening .temperature. Taking into account that the C/H ratio of the condensate was determined to be 0·95 and the molecular weight 270, it is suggested that the material may have a structure consisting of isolated aromatic rings fused into hydro-aromatic configurations, and containing aliphatic side chains limited in size to ethyl groups, and two molecular models with an empirical formula $C_{21}H_{22}$ are put forward for consideration. It is pointed out, however, that the solid condensate may represent more than a single substance.

W. E. WALKER, J. P. HENRY and H. G. DAVIS, of the Union Carbide Olefins Company, South Charleston, W.Va, described work on the titration of acidic functional groups in coal. It was found that titration of coal in ethylene diamine with sodium aminoethoxide titrant and in the presence of a weakly acidic substance such as carbazole gives a rapid and simple method for determining total acidity. The co-titration with carbazole gives sharper endpoints and higher titration values. After correcting for carboxyl content, a value for acidic hydroxyl is obtained agreeing well with the highest reproducible values reported by more specific methods of functional analysis. Besides carboxyl and phenols of several types, a number of functional groupings have been found to react as weak acids. Types not previously reported include certain polyphenols, indole and carbazole nitrogen, *n*-phenyl and α-phenyl amides and 1,2-benzfluorene.

TECHNICAL AUTHORSHIP

Regulations and syllabuses for a new scheme of courses and examinations in Technical Authorship have been drawn up by the City and Guilds of London Institute. The scheme of instruction is intended for those with engineering, technical or scientific training and experience, who wish to become technical authors. The course of instruction envisaged is a four-year part-time course. The Intermediate Examination of the Institute will be taken at the end of the second year of the course and the Final Examination at the end of the fourth year. These two examinations will be offered for the first time respectively in 1960 and 1961.

XXXIST INTERNATIONAL CONGRESS OF INDUSTRIAL CHEMISTRY

The thirty-first International Congress of Industrial Chemistry, organized jointly with the Federation of Chemical Industries of Belgium, will take place in Liège, Belgium, during 7 to 20 September 1958, it is announced by the Société de Chimie Industrielle of Paris.

Ten groups of subjects comprising some thirty separate sections are envisaged and of these Group II covers the following: Section 7—Solid and gaseous combustibles; Section 8—Liquid combustibles and petroleum products; Section 9—Petrochemistry. In addition it should be noted that Section 18 (Group VII) is concerned with powders and explosives (*Chairman*—P. L. GÉRARD).

All correspondence in connection with this Congress should be addressed in the first instance to the Sécrétariat général, 32 rue Joseph II, Bruxelles IV, or, during the period 6 to 12 September 1958, to the Palais des Congrès, Jardin d'Acclimatation, Liège.

W. A. KIRKBY

COMBUSTION AND FLAME

Readers of *Fuel* may like to know that *Notes* on the following subjects were included in the June 1958 issue of *Combustion and Flame*:

New design for boiler furnace
Cost of removal of sulphur dioxide from flue gases
Sampling of flame gases
Coal and coke fumes
Abatement of smoke from metallurgical furnaces
Burning velocity of coal-in-air suspensions
Radiation from luminous flames

OVERSEAS CORRESPONDENTS' NOTES

The Editor is grateful for the following information on matters of present interest relating to meetings and other activities in the fuel science field which have been supplied by (1) Dr H. R. Brown, and (2) Professor C. Padovani.

AUSTRALIA

A MAJOR Symposium on the Peaceful Uses of Atomic Energy, having particular reference to research and applications in Australia, was held in Sydney from 2 to 6 June 1958. About one hundred papers in all were presented—about 80 of these being of Australian origin.

The Conference was well supported by overseas participants. Mr GOTT, Dr FINNISTON and Mr FENNING of the U.K. Atomic Energy Authority presented papers dealing with the U.K. atomic energy programme in connection with power reactors now under construction, and with experience gained with research reactors at Dounreay and Calder Hall.

Other representatives from the United Kingdom were: Dr T. E. ALLIBONE and Mr A. L. SHAW from A.E.I. who dealt with the swimming pool reactor; Dr K. K. WOOTTEN of General Electric; Mr R. D. VAUGHAN, Nuclear Power Plant Company; Dr WOLFF, English Electric Company; and Mr W. R. WOOTTEN from Babcock & Wilcox who spoke on 'Nuclear steam power plant for waterless zones'.

There were quite a number from the United States of America, including: Mr C. C. VOGEL, Mr RODDIS, Dr E. J. LIEVEMANN, Dr J. E. COLE, Dr F. L. CUSTARD, Dr A. L. BAUGH, and Mr K. R. KRAMISH, who gave several papers dealing with the developments in atomic energy in America.

Dr E. G. HURST dealt with Canadian power reactors and Canadian research reactors.

Professor LLEWELLYN, Dr O'DELL, Dr HALL, from the University of Auckland, and Mr ROTH from the Dominion X-Ray and Radio Laboratory, Christchurch, were representatives from New Zealand.

In addition to the above, participants from Italy, Turkey, and other countries were expected.

The General Conference was under the Chairmanship of Professor J. P. BAXTER, Chairman of the Australian Atomic Energy Commission, and the Conference was divided into the following five sections:

(*1*) Materials section (raw materials, reactor materials)
(*2*) Power engineering section (power requirements, power reactors)
(*3*) Power auxiliaries section (fuel cycles, chemical processing, economics)
(*4*) Basic sciences section (nuclear physics and thermonuclear studies, reactor physics, radiochemistry)
(*5*) Associated techniques section (radioisotopes, active handling, instrumentation, health, nuclear education and training).

In connection with the Conference a comprehensive Exhibition of Atomic Energy was held in the Sydney Town Hall. Correspondence connected with the Symposium should be addressed to: The Symposium General Secretary, A.A.E.C. Research Establishment, Private Mail Bag, Sutherland, N.S.W., Australia.

ITALY

'L. Bocconi' Business University, Milan: International Economy of Power Sources

The 'L. Bocconi' University of Milan took the initiative some months ago of founding a special Institute of Economy of Power Sources. It is a self-governed organization, with the Hon. GIUSEPPE PELLA as President, and directed by a Steering Committee composed of Professors GIORDANO DELL'AMORE, CONSTANTINO BRESCIANI-TURRONI, LIVIO CAMBI, GIULIO DE MARCHI, LIBERO LENTI and ARMANDO SAPORI.

The principal purpose of this new Institute is to study and thoroughly investigate the important question of power, one of the most vital branches of economic studies.

The Institute, supported also by various private and public industrial enterprises, proposes to foster the study of power sources, and to disseminate information thereon. It is holding specialized university courses, and also organizes exchanges of material and contacts among economists and financiers in various countries.

The Institute is publishing a review *International Economy of Power Sources*, which carries reports and surveys by technicians and economists on the problems of production, distribution and consumption of power. So far two numbers have been published, from which we mention the following articles:

(*1*) O.E.E.C. and intra-European cooperation in the field of energy
(*2*) Studies in electronuclear power costs—L. GUATRI
(*3*) Legislation of power sources—R. NOBILI and G. ROSSI
(*4*) Energy situation in Italy in three years 1954, 1955, 1956—G. VERZI
(*5*) Energy and power supply—Sir J. ECCLES.

Letters to the Editor

Letters to the Editor on points of scientific interest related to fuel science are invited. The Editor does not hold himself responsible for opinions expressed in correspondence. Anonymous contributions cannot be accepted.

Carbon and Oxygen in Coals and Cokes

R. H. ESSENHIGH[1] has suggested the following relationship

$$[(O + S)/C]^{\frac{1}{2}} = K(100 + k - C) \quad \ldots\ [1]$$

where O, C and S are the oxygen, carbon and sulphur contents, respectively (dry, ash-free basis), of the coals and K and k are constants. We have examined this relationship for a series of some 190 coals and cokes. The coals covered a wide range of rank, the value of C varying from 65 to 95 per cent.

The plot of $[(O + S)/C]^{\frac{1}{2}}$ against C gave a good straight line. Visually, however, there seemed to be, for values of C greater than 90 per cent, either some increased scatter of points about the line or a different slope of the 'best' line. The same data were then used for a plot of $(O/C)^{\frac{1}{2}}$ against C. This also gave a good straight line, with a similar tendency for the high-rank materials. *Table 1* records the correlation data for the two relationships, based on 60 samples (arbitrarily selected) in each of the two rank-groups considered.

Table 1. Correlation data

Group	*Correlation of C with:*	*Correlation coefficient*	*Standard deviation of estimate*
Coals, C < 90%	$[(O + S)/C]^{\frac{1}{2}}$	−0·9880	0·0092
	$(O/C)^{\frac{1}{2}}$	−0·9956	0·0054
Coals, anthracites and cokes, C > 90%	$[(O + S)/C]^{\frac{1}{2}}$	−0·8109	0·0316
	$(O/C)^{\frac{1}{2}}$	−0·8632	0·0313

All the correlation coefficients are significant at the 99·9 per cent probability level, and the effect of including sulphur in the expression is not statistically significant, though Essenhigh stated that it removed certain anomalies. The increased standard deviation for the material of higher rank confirms the visual observation previously mentioned.

Essenhigh's thesis has certain features that call for comment. First, the choice of the organic compounds used to illustrate the relationship (*Figure 1* of Essenhigh's paper) is unfortunate; it would be possible to choose many organic compounds such as CH_3OH, $(COOH)_2$, $C_{10}H_7OH$, for which the points would not lie on the line. Despite the fact that the relationship involves the sulphur content, none of the five organic compounds chosen contains sulphur, but the point for sulphanilic acid ($HSO_3.NH_2C_6H_4$), for instance, would not lie on the line.

Mathematically, it is obvious that a strong relationship will hold between the two parameters, $[(O + S)/C]^{\frac{1}{2}}$ and C, since, in equation 1, the same variable, C, appears on both sides.

By ignoring the hydrogen and nitrogen contents the following relationship is obtained.

$$(O + S)/C \simeq (100 - C)/C \quad \ldots . [2]$$

Figure 1 shows this 'theoretical' relationship as applied to a plot of $[(O + S)/C]^{\frac{1}{2}}$ against C, for values of C from 20 to 100 per cent. For the range C = 50 per cent to C = 90 per cent, the relationship is substantially linear;

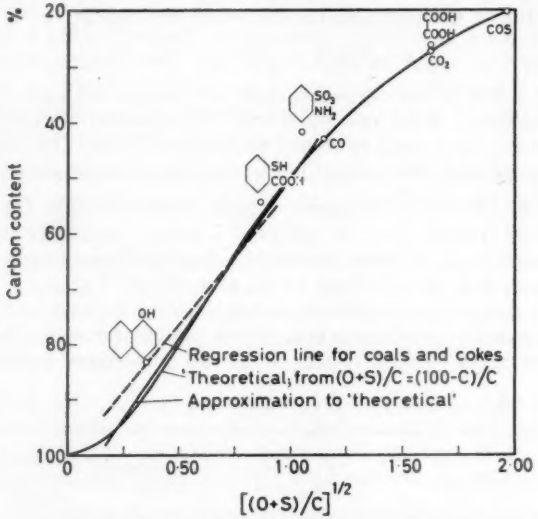


Figure 1. Relationships between $[(O + S)/C]^{\frac{1}{2}}$ *and* C

outside this range, smooth curves are obtained. *Figure 1* also shows the regression line calculated from our own data for coals having not more than 90 per cent of carbon (dry, ash-free basis). Examples of organic compounds which do not fall on the 'theoretical' line are also recorded. The deviation from linearity above C = 90 per cent explains the increased scatter observed for high-rank coals and cokes.

It is concluded that the Essenhigh's relationship is fictitious, as the two variables are not independent. H. BRIGGS[2] made a similar error, as has already been demonstrated[3].

We are grateful to the British Coke Research Association for permission to publish this letter.

J. M. RUCKLIDGE
W. C. THOMAS
H. C. WILKINSON

British Coke Research Association,
74 Grosvenor Street,
London, W.1

(*Received February 1958*)

REFERENCES

[1] ESSENHIGH, R. H. *Fuel, Lond.* 36 (1957) 395
[2] BRIGGS, H. *Colliery Engng* 8 (1931) 266; 9 (1932) 129
[3] MOTT, R. A. 'Coal Assessment'; summarized in *J. Inst. Fuel* 22 (1948) 2

On the Swelling of Steam-pretreated Brown Coal

EARLIER data[1] indicate the disappearance of the hysteresis of the water vapour adsorption isotherms for steam-pretreated lignite, contrary to raw lignite, for which the hysteresis is quite appreciable. During some investigations concerning the variation of volume of young brown coal with moisture, we also considered the problem of an eventual disappearance of the swelling hysteresis.

For this purpose we selected two average samples of the same brown coal, one raw and the other after dehydration by steam in an existing drying plant of Fleissner type. The selected brown coal had the following characteristics: ash content (dry basis) 10·56 per cent, carbon 64·7 per cent, hydrogen content 5·70 per cent and higher heating value (dry ash-free basis) 6220 kcal/kg.

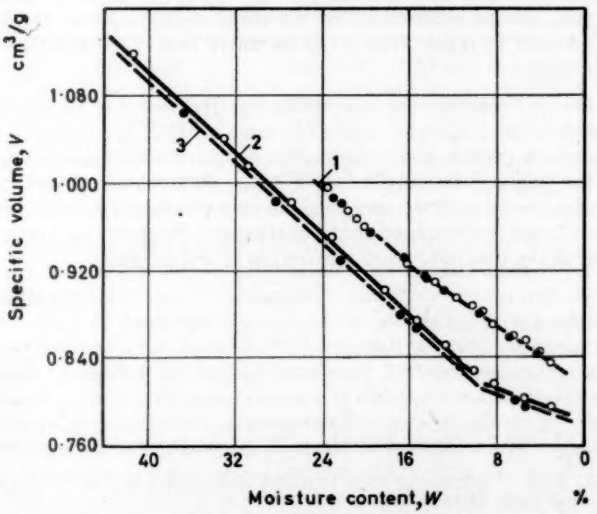


Figure 1. Variation of apparent specific volume with moisture. 1. Desorption and adsorption for steam-pretreated brown coal; 2. Desorption for raw brown coal; 3. Adsorption for raw brown coal

Both samples had been previously maintained in water for two hours. Afterwards different moisture contents of the coal were obtained in desiccators, over mixtures of sulphuric acid and water, at room temperature. The points on the adsorption curve (*Figure 1*) were obtained, after the coal had been dried, in the same manner up to *ca.* 3 per cent moisture. For each moisture content apparent specific volume of the coal was determined by a

special design of pyknometer with mercury. This pyknometer was filled with mercury under vacuum, at 0·05 atm and 20°C. Resulting data are shown in *Figure 1*, where both moisture contents and apparent specific volumes are referred to the dry basis of the coal. Moisture contents were determined by the indirect standard method of drying in air at 105°C.

From *Figure 1* and other measurements, the following conclusions may be drawn:

(*1*) For the same moisture content the apparent specific volume of the steam-pretreated coal is greater than that of the raw coal; this means that by steam-pretreatment new capillaries have been formed and at the same time some of those existing have been enlarged (and not collapsed, as at first assumed[1]).

(*2*) Although the specific volume of capillaries has been increased, the adsorption of water vapour by steam-pretreated coal is reduced in comparison with that of raw coal with the result that a great part of the capillaries do not retain water.

(*3*) The swelling–shrinking curves of the raw coal show hysteresis (of a constant value of 0·010 cm^3/g in the moisture range of 40 to 10 per cent); on the other hand for the steam-pretreated coal the hysteresis decreases so much, that it can be stated that it has practically disappeared.

This last fact confirms the assumption referring to one of the causes for the appearance of adsorptive hysteresis of natural coal[1,2], according to which in the desorption process some of the thin capillaries collapse, so that during adsorption they can no longer receive water. As a matter of fact, by steam-pretreating, the mass of the coal particles becomes more fixed (disappearance of the swelling hysteresis) and so the coal practically shows the same capillary structure at the desorption and adsorption of water vapour.

D. BUIMOVICI

Institute for Energetics of
the Academy of the R.P.R.,
Bucharest, Roumania

(*Received March 1958*)

REFERENCES

[1] LAVINE, I., GAUGER, A. W. and MANN, C. A. *Industr. Engng Chem.* (*Industr.*) 22 (1930) 1347
GAUGER, A. W. 'Condition of water in coals', in *Chemistry of Coal Utilization*, p 600. Wiley: New York, 1945

[2] ROSIN, P., RAMMLER, E. and KAYSER, A. G. *Braunkohle* 35 (1934) 289 and 305

*Aromaticity of Coal**

OPTICAL data due to J. SCHUYER and D. W. VAN KREVELEN[1] and X-ray measurements by H. E. BLAYDEN, J. GIBSON and H. L. RILEY[2], and by

* After this letter had been submitted to *Fuel*, a note was published [VAN KREVELEN, D. W., GROENEWEGE, M. P. and RIETVELD, B. J. *Nature, Lond.* 181 (1958) 640] in which was presented other evidence in disfavour of Friedel's suggestion that certain electronic absorption data indicated the low concentration of polynuclear aromatic structures in coal.

P. B. HIRSCH[3], together with fairly extensive chemical evidence have indicated that coal contains significant amounts of polynuclear aromatic structures. This conclusion is, however, challenged by R. A. FRIEDEL[4], who claims that it is not consistent with certain spectroscopic results. He quotes results for a Pittsburgh vitrain (84 per cent C) which had a specific extinction coefficient K (l/gcm) at 4920 Å of 5·6 compared with 200 for the polynuclear aromatic hydrocarbon violanthrene, and calculates that the vitrain could contain no more than 2·8 per cent violanthrene. Furthermore, from an inspection of K values of the principal absorption bands of some chosen organic compounds Friedel[4] concluded that the electronic absorption intensity of bituminous coals was too low to substantiate high concentrations of polynuclear aromatic compounds or of conjugated polyenes. Consequently he considered whether the dark colour of coal was due to the presence of free radicals or of charge complexes and concluded that the evidence favoured the former*.

Since extensive reassessment of past and present researches in coal chemistry would be necessary if it were firmly established that polynuclear aromatic structures are not indeed present in significant amount in coal, the author has examined Friedel's spectroscopic data in the light of further evidence.

Table 1. Comparison of spectral results

Compound	λÅ (*K max.*)	λÅ *max.* (*K max.*)
3,4-9,10-Dibenzpyrene[6]	2420 (330)	4330 (4)
1,2-4,5-Dibenzpyrene[6]	3070 (210)	4280 (7)
3,4-Benzpyrene[6]	2970 (250)	4030 (17)
1,2-Benzpyrene[6]	2890 (250)	3880 (1)
Various coal extracts[5]	~2300 (70–80)	~2600 (~60)

Table 1 compares spectral results of L. R. C. BARCLAY and T. M. LAYTON[5] relating to coal extracts with data obtained from spectral curves by E. CLAR[6] of some polynuclear aromatic hydrocarbons containing five and six condensed rings. The peaks of maximum intensity in the spectra of the aromatic hydrocarbons lie between 2420 Å and 3070 Å and have K values ranging from 210 to 330. The spectra of the coal extracts each contain two main peaks, the stronger near 2300 Å and the weaker near 2600 Å. Thus the weaker peaks in the spectra of the coal extracts occur in the wavelength range where the spectra of the polynuclear aromatic hydrocarbons have their strongest peaks. Calculation shows that if a similar method to that used by Friedel[4] to estimate violanthrene in coal is applied and if it is assumed that all the absorption of the coal extracts is due to the presence of benzpyrene- or dibenzpyrene-type structures then these could be present in the extracts to the extent of 18 to 29 per cent. Resemblances in the main features of the i.r. spectra of coal and of its various solvent extracts (C. G. CANNON and G. B. B. M. SUTHERLAND[7], I. G. C. DRYDEN and K. S. PANKHURST[8]) indicate that they contain similar basic skeletal units: therefore it may be assumed that the above calculated percentages of polynuclear aromatic structures in coal extracts apply equally to their parent coals. Furthermore, the benzpyrenes referred to in *Table 1* do

* In support of this view Friedel erroneously stated that coal is paramagnetic.

not absorb at all at 7000 Å and 4920 Å and only slightly at 4000 Å, these being the wavelengths at which Friedel examined the intensities of absorption of two coals. With coal, therefore, weak absorption at these wavelengths is no criterion for the absence of polynuclear aromatic structures.

The hydrocarbons that have been used in the above comparisons are unsubstituted, whereas any corresponding structures that may exist in coal would very probably contain many complex and possibly overcrowded substituents. In fact L. BLOM, L. EDELHAUSEN and D. W. VAN KREVELEN[9] have suggested that out-of-plane phenolic hydroxyl groups are present in coal: their presence could only be due to overcrowded substitution of aromatic nuclei. While it is known that overcrowded substituents may decrease electronic absorption intensities with respect to their parent hydrocarbons (M. S. NEWMAN[10]), the effect of uncrowded substituents on the absorption intensities of large polynuclear aromatic hydrocarbons is mainly unknown. However, results obtained by the present author have shown that di- and tetra-alkoxy-violanthrenes absorb about 33 per cent less intensely than does the parent violanthrene in the region of maximum wavelength of absorption. Thus it is apparent that the above calculated percentages of polynuclear aromatic structures in coal may be too low if the effect of their probable complex substitution is considered.

In conclusion, while it is admitted that electronic absorption data do not positively confirm the presence of polynuclear aromatic structures in coal or its extracts, on the other hand they do not reliably suggest their absence.

J. S. SHANNON

Commonwealth Scientific and Industrial Research Organization,
Coal Research Section,
P.O. Box 3,
Chatswood, New South Wales

(*Received April 1958*)

REFERENCES

[1] SCHUYER, J. and VAN KREVELEN, D. W. *Fuel, Lond.* 33 (1954) 176
[2] BLAYDEN, H. E., GIBSON, J. and RILEY, H. L. *Proc. Conf. Ultrafine Structure of Coals and Cokes*, p 176, British Coal Utilisation Research Association: London, 1944
[3] HIRSCH, P. B. *Proc. Roy. Soc. A* 226 (1954) 143
[4] FRIEDEL, R. A. *Nature, Lond.* 179 (1957) 1237
[5] BARCLAY, L. R. C. and LAYTON, T. M. *Fuel, Lond.* 35 (1956) 31
[6] CLAR, E. *Aromatische Kohlenwasserstoffe*, 2nd ed. Springer: Berlin, 1952
[7] CANNON, C. G. and SUTHERLAND, G. B. B. M. *Trans. Faraday Soc.* 41 (1945) 279
[8] DRYDEN, I. G. C. and PANKHURST, K. S. *Fuel, Lond.* 34 (1955) 363
[9] BLOM, L., EDELHAUSEN, L. and VAN KREVELEN, D. W. *Fuel, Lond.* 36 (1957) 135
[10] NEWMAN, M. S. *Steric Effects in Organic Chemistry* Wiley: New York, 1956

Acidic and Basic Groupings in Coal Tar Pitch

THERE is still doubt as to the manner in which the constituent compounds of coal tar pitch determine the physical properties of this substance. Earlier

workers (F. J. NELLENSTEIN[1]; E. J. DICKINSON[2]) were of the opinion that pitch had a colloidal structure, the colloidal particles resulting from the association of relatively simple compounds, whereas H. G. FRANCK[3] and L. J. WOOD and G. PHILLIPS[4] are more inclined to the view that pitches are mixtures of chemically similar substances whose physical properties are those of a solid solvate of cognate compounds in the form of a supercooled liquid, and that the colloid theory is not necessary. H. RAICH[5] and D. MCNEIL and G. A. VAUGHAN[6] have suggested that the properties of pitch could be explained by the existence of a state of dynamic molecular association, the pitch consisting essentially of labile swarms of associated molecules.

In two of the above theories it is implied that a significant proportion of the pitch consists of polar compounds. Of the more polar organic compounds, the ones most likely to occur in pitch would be phenols and heterocyclic tertiary bases. As is shown below, the concentrations of these in the pitch can be measured and their distribution in pitch fractions (obtained, for example, by solvent extraction) determined. The methods we have employed are based on the recent work of M. KATZ and R. A. GLENN[7] and of R. T. MOORE, P. MCCUTCHAN, and D. A. YOUNG[8], who applied direct non-aqueous potentiometric titration to the determination of phenolic-hydroxyl and basic-nitrogen groups in complex organic compounds.

For measuring phenolic-hydroxyl groups the apparatus was similar to that used by J. D. BROOKS and T. P. MAHER[9] in their studies of the acidic oxygen groups in coal and coal extracts. Small modifications were made to the apparatus—platinum was substituted for antimony in the reference electrode (because of ease of construction) and for the solvent pyridine was preferred to ethylene diamine as being less toxic. All determinations were carried out in an atmosphere of oxygen-free nitrogen. Addition of a measured amount of 2,6-xylenol to the sample was found to enhance the sharpness of the inflection at the end point.

Basic nitrogen was determined by perchloric acid titration of the sample dissolved or suspended in a mixture of glacial acetic acid and dioxane 2 : 1 v/v). Although this method determines all primary, secondary and tertiary amines, except those of the pyrrole type, the end point is marked by a single inflection. To shorten the procedure, recourse was had to back-titration with a standard base (quinoline) after the addition of an excess of perchloric acid to the sample.

Samples of medium-soft pitch, from representative New South Wales coke-oven and continuous-vertical-retort tars and from low-temperature tars obtained by a pilot-scale, 600°C, carbonization of a New South Wales gas coal and a Victorian brown coal, were prepared by the rapid distillation (70 g/min) of these tars in a metal still of the type described by the Standardization of Tar Products Test Committee[10]. Each pitch was divided, by treatment with solvents of increasing strength, into the following fractions:

(*1*) Soluble in light petroleum (b.pt 60 to 80°C)
(*2*) Insoluble in light petroleum, but soluble in benzene
(*3*) Insoluble in benzene, but soluble in pyridine
(*4*) Insoluble in pyridine.

Table 1

Sample	Tar type*	Pitch		Solvent analysis of pitch fraction as % w/w dry tar				Atomic C/H ratio				
		% w/w dry tar	Softening point K. & S. °C	Crystalloids	Resinoids	C_2	C_1	Pitch	Crystalloids	Resinoids	C_2	C_1
1	C.O.	62·4	71·0	20·9	19·5	6·2	14·9	1·70	1·40	1·62	1·57	2·17
2	C.V.R.	41·9	74·0	20·4	11·4	8·9	1·4	1·14	0·94	1·27	1·52	3·41
3	L.T.	44·3	64·5	22·6	10·6	10·6	*Nil*	1·10	0·97	1·13	1·30	—
4	L.T. (brown coal)	23·3	56·5	15·1	4·7	2·5	*Nil*	0·85	0·76	1·04	1·29	—

* C.O.—Coke oven; C.V.R.—Continuous vertical retort; L.T.—Low temperature.

Table 2

Sample	Phenolic OH %					Basic N %					Ratio: phenolic OH groups/basic N atoms					Equiv. wt assocd with each phenolic OH group			Mol. wts: determined by Wood and Phillips[4] on similar pitch fractions	
	Pitch	Cryst.	Resin.	C_2	C_1	Pitch	Cryst.	Resin.	C_2	C_1	Pitch	Cryst.	Resin.	C_2	C_1	Resin.	C_2	C_1	Resinoids	C_2
1	0·53	0·27	1·13	0·70	0·58	0·71	0·67	0·79	2·80	0·92	0·62	0·33	1·18	0·21	0·52	1500	2400	2900	613–656	1512–1752
2	1·50	1·26	2·13	1·47	0·70	0·99	0·63	1·52	1·58	0·31	1·25	1·65	1·15	0·77	1·86	800	1135	2500	717	1169
3	2·90	1·80	3·50	4·20	—	1·24	0·78	1·25	1·67	—	1·93	1·90	2·31	2·07	—	490	405	—	382	1017
4	1·24	1·16	2·45	2·45	—	0·43	0·20	0·82	1·06	—	2·37	4·80	2·46	1·90	—	700	700	—	—	—

These fractions are often referred to as 'crystalloids', 'resinoids', 'C_2' and 'C_1' respectively. Solvent analyses of the pitches examined are reported in *Table 1* on a per cent-dry-tar basis. Since pitches cannot be prepared under exactly equivalent conditions results on a per cent-pitch basis would be misleading.

The atomic C/H ratios of the pitch fractions (*Table 1*) follow the expected pattern—those of the coke-oven pitch fractions are high, those of the fractions from the waxy low-temperature brown coal tar pitch are low and those of the remaining pitches occupy an intermediate position.

The results of the functional-group analyses are given in *Table 2*. In the phenolic-hydroxyl determinations corrections were made for carbon dioxide in the solvent and traces of carboxylic acids in the sample (these gave a separate inflection in the titration curve). The functional groups in the C_1 fraction were determined on a suspension of this fraction in the appropriate solvent and the values may be low. Results of basic-nitrogen determinations on both C_1 and C_2 fractions were erratic owing to adsorption of pyridine by these fractions and the determinations were accordingly repeated on benzene-insoluble material (C_1 plus C_2) and on nitrobenzene-insoluble material (C_1 plus a little C_2) and the required values calculated.

The accuracy of the methods employed for functional group determinations was assessed by comparing the values obtained for each pitch by direct titration with the values calculated from the analyses of the separate pitch fractions. In most cases the difference was less than ten per cent.

The phenolic-hydroxyl content of the pitch fractions reaches a maximum in the resinoid fraction, except with pitch No. 3, whilst the maximum value for basic nitrogen occurs in the C_2 fractions. Other workers[4] have shown that, in general, there is a gradual increase in molecular weight with decreasing solubility of fractions from coke-oven and vertical-retort pitches. The possible divergence in the trends of phenolic-hydroxyl content and molecular weight with decreasing solubility of pitch fractions would not be in accord with the view that pitch consists of continuous series of homologous compounds. Furthermore, the phenolic-hydroxyl content of the resinoid and C_2 fractions is such that the equivalent weights associated with each hydroxyl group are of the same order as the molecular weights determined osmometrically on similar materials by Wood and Phillips[4] (*Table 2*).

Whilst it is unlikely that each of the constituent molecules of the resinoid and C_2 fractions contains a single phenolic-hydroxyl group, the hydroxyl values obtained do indicate that this functional group may contribute to the physical properties of the pitch fractions and of the pitch itself; and even in pitches from high-temperature tars it is by no means a negligible factor as has been suggested[3].

The ratios of the number of phenolic groups to basic-nitrogen atoms in each fraction are given in *Table 2*. For the resinoids, C_2 and C_1 fractions the ratios lie between 0·21 and 2·46 and it is clear that if base–phenol association occurs a high proportion of the phenolic-hydroxyl groups and basic-nitrogen atoms could be involved in the association complex.

The results of the investigation to date will be of value in further studies of pitch structure and of the weathering and air-blowing of pitches. The distribution and concentration of phenolic-hydroxyl groups and basic nitrogen in the pitch fractions (*Table 2*) indicate that coal tar pitches are solutions of as-yet unidentified, medium-molecular-weight polar compounds in relatively non-polar solvents. These solvents correspond, approximately, to the crystalloid fraction and consist of higher homologues of the constituents of the tar distillate. It remains to be established how these polar molecules are disposed in the solution.

The authors wish to thank Mr J. D. Brooks for his interest and helpful suggestions.

E. J. GREENHOW
J. W. SMITH

Commonwealth Scientific and Industrial Research Organization, Coal Research Section, P.O. Box 3, Chatswood, New South Wales

(*Received April 1958*)

REFERENCES

[1] NELLENSTEIN, F. J. *Teer (u. Bitum.)* 31 (1933) 309
[2] DICKINSON, E. J. *J. Soc. chem. Ind., Lond.* 64 (1945) 121
[3] FRANCK, H. G. *BrennstChemie* 36 (1955) 12
[4] WOOD, L. J. and PHILLIPS, G. *J. appl. Chem.* 5 (1955) 326
[4] RAICH, H. Koppers Fellowship at Mellon Institute 1952 (ref. in O'BROCHTA, J. *Composition and Properties of Coal Tar Pitches*, p 18. Koppers Co. Inc.: Pittsburgh, 1956)
[6] MCNEIL, D. and VAUGHAN, G. A. *Instn Gas Engrs, Lond., Publ. No. 438/219* (1953) 6
[7] KATZ, M. and GLENN, R. A. *Analyt. Chem.* 24 (1952) 1157
[8] MOORE, R. T., MCCUTCHAN, P. and YOUNG, D. A. *Analyt. Chem.* 23 (1951) 1639
[9] BROOKS, J. D. and MAHER, T. P. *Fuel, Lond.* 36 (1957) 51
[10] *Standard Methods for Testing Tar and its Products*, 3rd ed. Standardization of Tar Products Test Committee: London, 1950

Formation of Chloroform-soluble Material in Coking Coal

DURING investigations into the formation of chloroform-soluble material in coking coals during carbonization[1] it was observed that replicate measurements of the proportions of chloroform-solubles (by extraction in Soxhlet apparatus) would occasionally differ from each other by far more than the normal experimental error incurred in the measurement. While determinations on chars prepared at $< 400°C$ and $> 425°C$ tended to be rather precise, replicates for chars carbonized at temperatures *between* 400° and 425°C would, in extreme cases, deviate from the arithmetic mean by as much as ± 25 per cent.

These deviations appear to arise from complexities associated both with the formation and the subsequent decay of the chloroform-soluble material. Experiments carried out in these laboratories suggest that satisfactory agreement between replicates over the whole temperature range can be secured

when the coal is carbonized at high rates and the soaking period kept short; but the single maximum of the plot of chloroform-solubles versus carbonization temperature is then resolved into two peaks that may be separated by as little as 15°C. It is therefore probable that formation and later disappearance of the chloroform-soluble complex either each involve at least two consecutive reactions, or that the rates of the formative and destructive reactions —and any metastable equilibria between them—are critically dependent upon

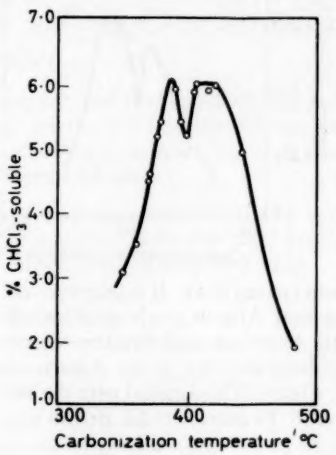


Figure 1. Variation of chloroform-solubles with carbonization temperature; Crowsnest Pass coal, −200 mesh

temperature, upon the rate at which the reaction temperature is approached, and upon the period of time for which the reaction temperature is maintained. The previously reported single maximum in the plot of chloroform-solubles versus carbonization temperature (and the excessive differences between replicates noted in the present studies) may be connected with the apparent merging of the several reactions under particular experimental conditions.

Figure 1 illustrates some typical results obtained when a coking coal is extracted with chloroform after carbonization at 20°C/min. The coal with which the data in this diagram were recorded was a medium-volatile bituminous coal from the Crowsnest Pass area of S.W. Alberta (C = 87·8 per cent, H = 5·4 per cent, d.a.f.; B.S. Swelling Number ~ 8), ground to pass a 200 mesh screen, carbonized in a rapid stream of oxygen-free nitrogen, and in each instance held at the final temperature for 5 minutes. Carbonization was carried out in small porcelain boats inserted into an electrically-heated furnace; control over temperatures and the rate of heating was effected by means of electronic recording gear previously described[2]. At the end of the 5-minute soaking period, the samples were withdrawn from the furnace and rapidly cooled in nitrogen. Extraction of the carbonized residues with chloroform was carried out in open Soxhlet apparatus at the boiling point of the solvent for a period of 72 hours, i.e. until no further discoloration of the solvent was observed for several hours. The chloroform-solutions were then condensed by distillation, and the condensed solutions evaporated to dryness

(and constant weight) in a vacuum oven. The drying temperature was in the region 65° to 70°C.

Similar 'splitting' of the single peak of the plot of chloroform-solubles versus carbonization temperature has been found when working with the Crowsnest Pass coal ground to −65+200 mesh (*Figure 2*) and with two other

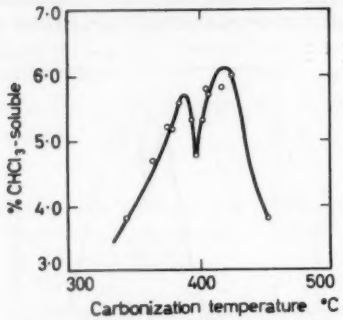


Figure 2. Variation of chloroform-solubles with carbonization temperature; Crowsnest Pass coal, −65+200 mesh

Alberta coking coals. It is therefore unlikely to be a 'freak effect'. It should be noted that Alberta coals conform closely to the systematics applicable to North American and Western European coals[3] and that the variation of chloroform-solubles in an Alberta non-coking coal (from the Drumheller area; *Figure 3*) is identical with the variations established by I. G. C. DRYDEN and K. S. PANKHURST[1] for British coals of the same type.

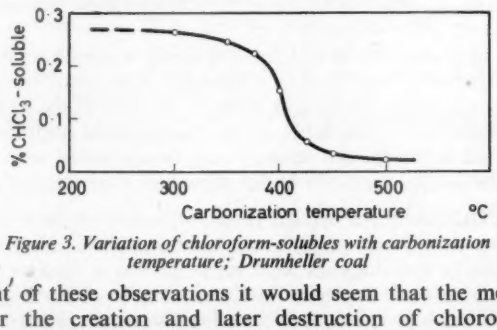


Figure 3. Variation of chloroform-solubles with carbonization temperature; Drumheller coal

In the light of these observations it would seem that the mechanism responsible for the creation and later destruction of chloroform-soluble material in a coking coal is considerably more complex than has been envisaged. While available data are still scanty (and, in their present form, unsuitable for an elucidation of the kinetics of the process), there can be little doubt that formulations of the overall carbonization process in terms of a series of first-order reactions[4,5] represent a simplification that can offer little detailed knowledge about the course of carbonization. At best, such formulations mirror a statistical average behaviour.

W. DEN HERTOG
N. BERKOWITZ

Research Council of Alberta,
Edmonton, Canada

(*Received April 1958*)

REFERENCES
[1] DRYDEN, I. G. C. and PANKHURST, K. S. *Fuel, Lond.* 34 (1955) 363
[2] BERKOWITZ, N. *Fuel, Lond.* 36 (1957) 355
[3] BERKOWITZ, N. *Canad. J. Technol.* 33 (1955) 169
[4] CHERMIN, H. A. G. and VAN KREVELEN, D. W. *Fuel, Lond* 36 (1957) 85
[5] FITZGERALD, D. *Trans. Faraday Soc.* 52 (1956) 362

Kinetics of Fluidity of Coal and the Chloroform-soluble Extract

AN article[1] was published in the January issue of *Fuel* in which the authors gave an account of work carried out on the yield of chloroform-soluble extract from a plasticized bituminous coal and its relation to the maximum fluidity of coal as determined by the Gieseler method.

The results from this very interesting investigation allowed the authors to conclude that this extract cannot be identified with the 'fluid coal' and that it does not determine the kinetics of the phenomenon of fluidity.

Table 1. Coal characteristics

Code No.	*Plasticity temperatures by Gieseler*			*Maximum fluidity*
	$t_{soft.}$	$t_{max.}$	$t_{resol.}$	
634	365	431	473	6060

I present here some of the results of my investigations on the same problem which are being carried out in our laboratory.

These results seem to show that a relation exists between the yield of the chloroform-soluble extract and other properties of the coal investigated, although the conditions of experimentation which we have used were quite different from those to which reference has been made.

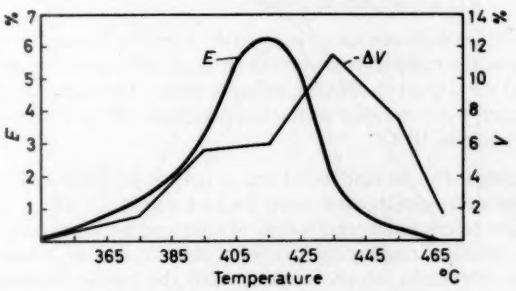


Figure 1. Amount of extract (E) and loss of weight (ΔV) at different temperatures of plasticizing

We have plasticized 10 g of coal in an iron tube of 16 mm diameter. The coal samples were heated in a salt-bath with a heating rate of 3°/min to the different temperatures of the plastic range (*Table 1*). After reaching the necessary temperature the coal sample was maintained for 5 minutes at this temperature and then rapidly cooled.

After weighing, the sample was extracted by chloroform at about 40°C.

Figure 1 shows the amounts of extract obtained from the coal samples plasticized at the different temperatures. We have plotted on the same figure the differential curve of the loss of weight of the coal sample due to the escape of the decomposition gases against the temperatures of plasticizing.

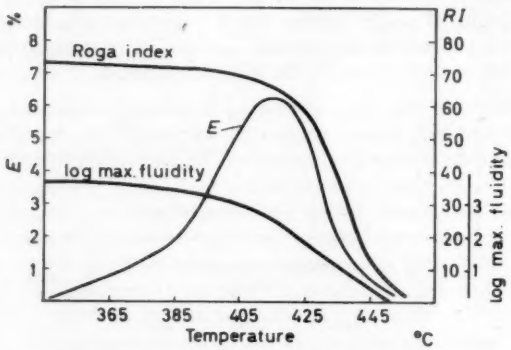


Figure 2. The relation between log maximum fluidity and Roga Index of plasticized coal and the yield of extract at different temperatures

It may be noted that the increase in the yield of the extract is connected with a delay in the degasification and vice versa the decrease takes place in the same temperature range when the degasification has reached its maximum.

We have investigated changes of other properties of the same plasticized coal samples. The maximum fluidity (by Gieseler) and the caking property (Roga Index—*RI*) are shown in *Figure 2*.

The correlation between these properties seems to be supported by *Figure 3*, which shows the relation between the amount of chloroform-soluble extract and the (log) maximum fluidity of different coals. The samples of these coals were plasticized for 5 minutes at the temperatures of their maximum fluidity (by Gieseler) minus 10°C.

Summarizing it can be concluded that it is very probable that the plasticity of bituminous coals can be accounted for by a substance which is formed as a product of the primary decomposition of coal and which can be extracted by chloroform without employing pressure and at a low temperature. The residue after extraction ceases to show both the plastic behaviour and the caking properties in spite of the fact that we can obtain from it a further 7 to 9 per cent of extract using pyridine as a solvent.

We have found an interesting correlation between the yield of extract by chloroform and the pressure exerted on the coal sample during plasticizing. The escape of the decomposition gases is prevented to some extent by the pressure.

Figure 4 shows the results obtained in these measurements.

As we see from these coal samples plasticized at higher pressure more extract is obtained. This clearly follows assuming with D. W. VAN KREVELEN[2]

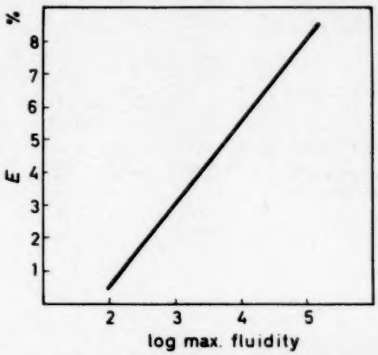


Figure 3. The relation between the amount of extract and log maximum fluidity of different coals

that the plastic state of bituminous coals is a result of two opposite reactions:

(*1*) coal ⟶ metaplast (liquid)

(*2*) metaplast ⟶ semicoke (solid).

Reaction 2 is connected with an evolution of gaseous products of the decomposition of the metaplast. The pressure holds back reaction 2 and could be without influence on reaction 1.

This statement throws an interesting light on the role of the expansion pressure of the coal, the physicochemical aspects of its action during coking and its advantageous influence on the quality of coke[3].

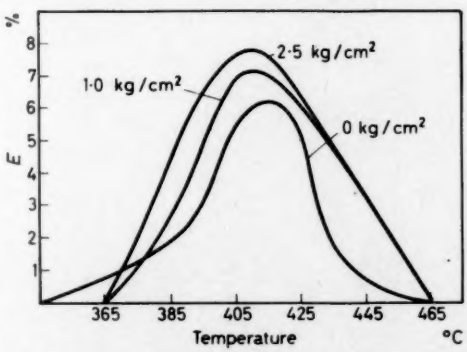


Figure 4. The relation between the yield of extract and the pressure during plasticizing

In relation to the last fact it seems to me, that the method of heating the coal samples in the fluid bed, as performed by the authors of the first-mentioned article, does not permit comparison between the results obtained using the extraction and the plasticity measurement by the Gieseler method, because the heating conditions employed in the two methods are quite different.

J. NADZIAKIEWICZ

Institute for Chemical Utilization of Coal, Zabrze, Poland

(*Received May 1958*)

REFERENCES

[1] OXLEY, G. R. and PITT, G. J. *Fuel, Lond.* 37 (1958) 19
[2] VAN KREVELEN, D. W. *BrennstChemie* 37 (1956) 101
[3] NADZIAKIEWICZ, J. (*Prace*) *Komun. No. 162.* Głównego Instytutu Górnictwa: Katowice, 1954